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Physics. — P. EHRENFEST and G. E. UHLENBECK: *"On the connection of different methods of solution of the wave equation in multi-dimensional spaces".*

(Communicated at the meeting of April 24, 1926).

Introduction.

The general equation for wave motion in space under the influence of an external force $k\,(t, x\,y\,z)$:

$$\frac{1}{c^2}\frac{\partial^2 s}{\partial t^2} - \Delta s = k(t, xyz)$$

has, when for $t = -\infty$ everything is at rest $\left(s_{t=-\infty} = \left(\frac{\partial s}{\partial t}\right)_{t=-\infty} = 0\right)$, the well known solution, the retarded potential:

$$s = \frac{1}{4\pi}\int\!\!\int\!\!\int_{-\infty}^{+\infty} \frac{k(t-\frac{r}{c}, \xi\eta\zeta)}{r}\, d\xi d\eta d\zeta.$$

The pecularities of this solution, especially its close connection to the three dimensional space, become apparent when we consider the analogous problem for the wave equation in multidimensional spaces:

$$\frac{\partial^2 s}{\partial t^2} - \sum_{h=1}^{n} \frac{\partial^2 s}{\partial x^2_h} = k(t, x_1 \ldots x_n) \; . \; . \; . \; . \; . \; . \; . \qquad (1)$$

Various methods are available, but they all give the solution in *very different* analytical forms, whose identity unlike the case with three dimensions is not at once clear. In the following we will endeavour to show the connection and the identity of these solutions. [1]) The difference between spaces with an even and an odd number of dimensions will be especially brought to the front. [2])

§ 1. *Method of* HERGLOTZ [3]).

Putting $t = i\omega$, in (1), then the latter is transformed to the equation of POISSON in $n+1$ dimensions. Now the use of the known solution for this, suggests in our case the trial of:

$$s(t, x_1 \ldots x_n) = \frac{\Gamma\left(\frac{n-1}{2}\right)}{2\pi^{\frac{1}{2}n-\frac{1}{2}}} \int_{-\infty}^{+\infty}\!\!\ldots\!\int d\xi_1 \ldots d\xi_n \cdot \frac{1}{2\pi i}\int_{-\infty i}^{+\infty i} \frac{k(t-\vartheta, \xi_1 \ldots \xi_n)}{(r^2-\vartheta^2)^{\frac{n-1}{2}}}\, d\vartheta \quad . \qquad (2)$$

as a solution. By transforming the integration path of the last integral, we can write it without complex variables. Here enters the difference between spaces with even and odd numbers of dimensions.

a. When n is *odd* (put $n = 2p + 3$), we transform the path of integration to a small circle round one of the poles $\vartheta = + r$ or $\vartheta = - r$ of the integrand, and obtain with the help of the theorem of residues the solution represented by a "retarded" or an "advanced" potential respectively. In the first case for example:

$$s(t, x_1 \dots x_{2p+3}) = \frac{\Gamma(p+1)}{2\pi^{p+1}} \int_{-\infty}^{+\infty} \dots \int d\xi_1 \dots d\xi_{2p+3}\, H_{2p+3} \quad . \quad . \quad (3)$$

is obtained, where:

$$H_{2p+3} = \frac{1}{p!} \sum_0^p l \frac{(2p-l)!}{l!\,(p-l)!} \cdot \frac{1}{2^{2p-l+1}} \frac{k^{(l)}(t-r, \xi_1 \dots \xi_n)}{r^{2p-l+1}} \quad . \quad . \quad . \quad (4)$$

b. When n is *even* (put $n = 2q$), we can no longer close the integration path, as $\vartheta = \pm r$ are now also branching points, and we can only transform it to a loop round $\vartheta = + r$ or $\vartheta = - r$. The real expressions can now be written with the help of the so called "partie finie" of an infinite integral, as defined by HADAMARD.4) We obtain:

$$s(t, x_1 \dots x_{2q}) = \frac{\Gamma\left(q - \frac{1}{2}\right)}{2\pi^{q-\frac{1}{2}}} \int_{-\infty}^{+\infty} \dots \int d\xi_1 \dots d\xi_{2q}\, H_{2q} \quad . \quad . \quad (5)$$

where

$$H_{2q} = \frac{(-1)^q}{\pi} \left|\overline{\int_r^\infty d\vartheta \frac{k(t-\vartheta, \xi_1 \dots \xi_{2q})}{(\vartheta^2 - r^2)^{q-\frac{1}{2}}}}\right. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

the bracket indicating the "partie finie". This becomes then in ordinary symbols:

$$H_{2q} = \frac{(-1)^q}{\pi} \int_r^\infty \frac{f(\vartheta) - \left[f(r) + (\vartheta - r) f'(r) + \dots + \frac{(\vartheta - r)^{q-2}}{(q-2)!} f^{(q-2)}(r)\right]}{(\vartheta - r)^{q-\frac{1}{2}}} \quad (7)$$

where:

$$f(\vartheta) = \frac{k(t-\vartheta)}{(\vartheta + r)^{q-\frac{1}{2}}}$$

Remarks:

1. If the solution for a certain n is known, then the solution for $n - 1$ can always be found by the consideration of the cylindrical problem (the so called "methode de la descente" of HADAMARD). Formula (6) can be derived in this way from the solution (3).
2. The application of this method to (2) gives the solution in one dimension lower again in exactly the same form.
3. Still (2) and the transformations of the integration path indicated under *a* and *b* must only be considered as a heuristic method of arriving at the real expressions (3) and (5), which as can be shown are really

the solutions of our problem. It is difficult to give the exact meaning of (2) and the justification of the transformations.

§ 2. *"Polarisationmethod"*. [5]

Physically the solution of our problem can be represented as the superposition of all the „spherical waves" excited in the various points of the phase space by the „force" $k(t, x_1 \ldots x_n)$. It can be easily shown [5] that, in analogy to $\frac{\Phi(t-r)}{r}$ for three dimensions, a solution of the equation for spherical waves in $(2p+3)$ dimensions is given by:

$$u_{2p+3} = \left(\frac{1}{r}\frac{\delta}{\delta r}\right)^p \frac{\Phi(t-r)}{r} \quad \ldots \ldots \ldots \quad (8)$$

which at once suggests as a solution:

$$s(t, x_1 \ldots x_{2p+3}) = A_{2p+3} \int_{-\infty}^{+\infty} \ldots \int d\xi_1 \ldots d\xi_{2p+3} \left(\frac{1}{r}\frac{\delta}{\delta r}\right)^p \frac{k(t-r, \xi_1 \ldots \xi_{2p+3})}{r} \quad (9)$$

Here A_{2p+3} is a constant. The solution is essentially limited to an *odd* number of dimensions.

The identity of (9) and (3) can be shown as follows:

Let:

$$P_{2p+3} = \left(\frac{1}{r}\frac{\delta}{\delta r}\right)^p \frac{k(t-r)}{r} \quad \ldots \ldots \ldots \quad (10)$$

From the definition of H_n:

$$H_3 = \frac{1}{2\pi i}\int d\vartheta \frac{k(t-\vartheta)}{r^2-\vartheta^2} = \frac{1}{2}\frac{k(t-r)}{r} = \frac{1}{2} P_3$$

and therefore

$$\left.\begin{aligned} P_{2p+3} &= \left(\frac{1}{r}\frac{\delta}{\delta r}\right)^p \frac{k(t-r)}{r} = \left(\frac{1}{r}\frac{\delta}{\delta r}\right)^p (2H_3) = \\ &= \frac{1}{\pi i}\int d\vartheta \frac{k(t-\vartheta)}{(r^2-\vartheta^2)^{p+1}}\, 2^p (-1)^p p! = (-1)^p 2^{p+1} p!\, H_{2p+3} \end{aligned}\right\} \quad . \quad (11)$$

Equation (11) can also be derived by direct differentiation, H_{2p+3} then being given by (4). From (3) and (11) then follows the constant in (9):

$$A_{2p+3} = \frac{(-1)^p}{2^{p+2}\pi^{p+1}} \quad \ldots \ldots \ldots \ldots \quad (12)$$

§ 3. *Method of* RIEMANN-HADAMARD [6].

This method starts from the identity of GREEN, and is therefore in many ways analogous to the usual method of solving POISSON's equation. Hence in our case it is actually not very different from the method of HERGLOTZ, except that now everything is kept real from the beginning.

HADAMARD, however, has applied it to much more general hyperbolic equations and boundary conditions. Specialising his results to our problem then:

a) for an *even* number of dimensions ($n=2q$)[7]:

$$s(t, x_1 \ldots x_{2q}) = \frac{(-1)^{q+1}\Gamma(q-\frac{1}{2})}{2\pi^{q+\frac{1}{2}}} \left|\overline{\int\cdots\int_T \frac{1}{\Gamma^{q-\frac{1}{2}}} k(\tau, \xi_1 \ldots \xi_{2q})\, d\xi_1 \ldots d\xi_{2q} d\tau}\right. \quad (13)$$

where:

$$\Gamma \equiv (t-\tau)^2 - \sum_1^{2q} (x_h - \xi_h)^2 = (t-\tau)^2 - r^2$$

and T is the cone $\Gamma = 0$. Putting $t-\tau=\vartheta$, we get (5) and (6), i. e. the solution of HERGLOTZ for an even number of dimensions.

b) for an *odd* number of dimensions ($n=2p+3$)[8]:

$$s(t, x_1 \ldots x_{2p+3}) = \frac{(-1)^{p+1}}{2\pi^{p+1}} \lim_{\gamma \to 0} \left[\frac{d^p}{d\gamma^p} \int\cdots\int_\sigma k(\tau, \xi_1 \ldots \xi_{2p+3})\, d\sigma\right] \quad (14)$$

where σ represents the surface of the hyperboloid:

$$\Gamma \equiv (t-\tau)^2 - r^2 = \gamma$$

and the element $d\sigma$ thereof is defined by:

$$d\sigma d\Gamma = d\xi_1 \ldots d\xi_{2p+3}\, d\tau.$$

Hence:

$$d\sigma = -\frac{d\xi_1 \ldots d\xi_{2p+3}}{2(t-\tau)} = -\frac{d\xi_1 \ldots d\xi_{2p+3}}{2\sqrt{r^2+\gamma}}$$

$$\tau = t - \sqrt{r^2+\gamma}$$

$$s(t, x_1 \ldots x_{2p+3}) = \frac{(-1)^p}{4\pi^{p+1}} \lim_{\gamma \to 0} \left[\frac{d^p}{d\gamma^p} \int_{-\infty}^{+\infty}\cdots\int d\xi_1 \ldots d\xi_{2p+3} \frac{k(t-\sqrt{r^2+\gamma})}{\sqrt{r^2+\gamma}}\right] =$$

$$= \frac{(-1)^p}{2^{p+2}\pi^{p+1}} \lim_{\gamma \to 0} \left(\frac{\delta}{r\delta r}\right)^p \int_{-\infty}^{+\infty}\cdots\int d\xi_1 \ldots d\xi_{2p+3} \frac{k(t-\sqrt{r^2+\gamma})}{\sqrt{r^2+\gamma}}$$

$$= \frac{(-1)^p}{2^{p+2}\pi^{p+1}} \int_{-\infty}^{+\infty}\cdots\int d\xi_1 \ldots d\xi_{2p+3} \left(\frac{\delta}{r\delta r}\right)^p \frac{k(t-r)}{r}.$$

We thus get the polarisationsolution (9).

§ 4. *Method of* FOURIER-POISSON[9].

From the identity of FOURIER, we have:

$$k(t, x_1 \ldots x_n) = \frac{1}{(2\pi)^n} \int_{-\infty}^{+\infty}\cdots\int dv_1 \ldots dv_n \int_{-\infty}^{+\infty}\cdots\int d\xi_1 \ldots d\xi_n e^{i\Sigma v_h(x_h-\xi_h)} k(t, \xi_1 \ldots \xi_n). \quad (15)$$

Similarly we now *put* for the solution:

$$s(t, x_1 \ldots x_n) =$$

$$= \frac{1}{(2\pi)^n} \int_{-\infty}^{+\infty} \!\!\ldots\! \int d\nu_1 \ldots d\nu_n \int_{-\infty}^{+\infty} \!\!\ldots\! \int d\xi \ldots d\xi_n e^{i\Sigma \nu_h (x_h - \xi_h)} H(t, \xi_1 \ldots \xi_n, \nu_1 \ldots \nu_n) \quad (16)$$

where $H(t, \ldots \xi_1 \ldots \xi_n, \nu_1 \ldots \nu_n)$ is an *unknown* function. Substituting (15) and (16) in (1), we get for H the equation:

$$\frac{\delta^2 H}{\delta t^2} + \nu^2 H = k(t, \xi_1 \ldots \xi_n) \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where $\nu^2 = \sum_1^n \nu_h^2$. With the limiting values $H_{t=-\infty} = \left(\frac{\partial H}{\partial t}\right)_{t=-\infty} = 0$, we get:

$$H = \int_{-\infty}^{t} d\tau \, \frac{\sin \nu(t-\tau)}{\nu} \, k(\tau, \xi_1 \ldots \xi_n).$$

as the solution of (17).

This in (16) gives the required solution. If we introduce polar coordinates into the ν-space, then we can easily perform all the integrations except those over the radiusvector ν and one angle γ $\left[\text{defined by } \cos \gamma = \sigma = = \frac{1}{\nu r} \Sigma \, \nu_h (x_h - \xi_h)\right]$. Also putting $t - \tau = \vartheta$, then:

$$s(t, x_1 \ldots x_n) = \frac{n-1}{2^{n-1} \pi^{\frac{1}{2} n + \frac{1}{2}} \Gamma\left(\frac{n+1}{2}\right)} \int_{-\infty}^{+\infty} \!\!\ldots\! \int d\xi_1 \ldots d\xi_n \, F_n \quad . \quad (18)$$

where:

$$F_n = \int_0^\infty d\nu \nu^{n-2} \int_0^\infty d\vartheta \sin \nu\vartheta k(t-\vartheta, \xi_1 \ldots \xi_n) \int_0^1 d\sigma (1-\sigma^2)^{\frac{n-3}{2}} \cos \nu r \sigma \quad . \quad (19)$$

For an *odd* number of dimensions the identity of (18) with (3) and (4) can be shown by direct calculation of (19). For optional values of *n* the demonstration of the identity with (2) can also be given (perhaps not mathematically irreproachable *)) as follows: The comparison of (2) with (18) and (19) shows, that we must demonstrate:

$$\left.\begin{aligned} &\frac{1}{2\pi i} \int_{-\infty i}^{+\infty i} \frac{k(t-\vartheta)}{(r^2-\vartheta^2)^{\frac{n-1}{2}}} \, d\vartheta = \\ &= \frac{1}{2^{n-3} \pi \Gamma^2\left(\frac{n-1}{2}\right)} \int_0^\infty d\nu \nu^{n-2} \int_0^\infty d\vartheta \sin \nu\vartheta k(t-\vartheta) \int_0^1 d\sigma \, (1-\sigma^2)^{\frac{n-3}{2}} \cos \nu r \sigma \end{aligned}\right\} \quad (20)$$

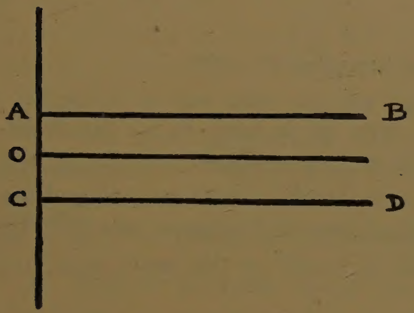
---

*) In the transformations of the integration paths we have the same incertainties as in § 1. (See remark 3).

We start from the identity ($\alpha > o$):

$$\int_0^\infty d\nu\,\nu^{n-2} e^{-\alpha\nu} \int_0^1 d\sigma (1-\sigma^2)^{\frac{n-3}{2}} \cos \nu r\sigma = \frac{2^{n-3}\Gamma^2\left(\frac{n-1}{2}\right)}{(r^2+\alpha^2)^{\frac{n-1}{2}}} \quad . \; . \; . \quad (21)$$

Now putting in (20) $\sin \nu\vartheta = \frac{1}{2i}\,(e^{i\nu\vartheta} - e^{-i\nu\vartheta})$, we can divide the right hand side into two integrals. Instead of the interval $(0.\infty)$ we now take in the first integral for ϑ the path *OAB*, and in second the path *OCD*. Changing in each integral the integration over ϑ with that over ν, then the resulting integrals are convergent and can be calculated by (21). Finally, by combining both integrals into one over the loop *DCAB*, (20) is demonstrated.



LITERATURE AND FURTHER REMARKS.

1. The analogue for the equation of heat conduction has recently been shown by M. C. GRAY (Proc. Edinb. Roy. Soc. XLV, 230, 1925).

2. The principle of HUYGENS is, as is well known, no longer valid in spaces of an even number of dimensions. See for two dimensions RAYLEIGH, The Theory of Sound (Sec. edition 1896) Vol. II, Ch. XIV, § 275, and for further differences: P. EHRENFEST: In what way does it become manifest in the fundamental laws of physics, that space has three dimensions? Proc. Acad. Amst. **20**, 200, 1917.

3. HERGLOTZ: Gött. Nachr. p. 549, 1904.

4. HADAMARD: Acta Math. **31**, 339, 1908; Lectures on Cauchy Problem (London, Humphrey Milford, 1923) p. 133.

5. Comp. J. COULON: Sur l'intégration des équations aux dérivées partielles par la méthode des caractéristiques (Paris, Hermann, 1902) p. 56.

6. RIEMANN: Ueber die Fortpflanzung ebener Luftwellen von endlicher Schwingungsweite. Ges. Werke p. 157.

KIRCHHOFF: Zur Theorie der Lichtstrahlen. Ges. Abh., Nachtrag No. 3, p. 22.

VOLTERRA: Atti Lincei 1892; Acta Math. **18**, 214, 1894.

TEDONE: Annali di Mathematica, Serie 3, T. **1** (1898) p. 1.

HADAMARD: Ann. Sc. de l'Ec. Norm. Sup. **21**, 535, 1904; **22**, 101, 1905.
Journ. de Phys. 1906 (survey); Acta Math. **31**, 333, 1908.

HADAMARD has given a survey of all these researches in his book: Lectures on Cauchy Problem in linear' hyperbolic partial differential equations (London, Humpfrey Milford, 1923). This is cited below.

7. Follows from form. (39), p. 166 l.c.

8. Follows from form. (28), p. 232 l.c., which is got by the „méthode de la descente" from form. (39) p. 166.

9. For the papers of POISSON, see: H. BURKHARDT, Entwicklung nach oscillierenden Funktionen (Teubner, 1908) p. 606. Comp. further: RAYLEIGH, Theory of Sound (Sec. Edit. 1896), Ch. XIV. RIEMANN-HATTENDORF, Partielle Differentialgleichungen § 106.

Chemistry. — *"The Scattering Power of Lithium and Oxygen, Determined from the Diffraction-Intensities of Powdered Lithiumoxide".* By J. M. BIJVOET, A. CLAASSEN and A. KARSSEN. (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of September 25, 1926).

1. Li_2O crystallizes in the Fluor-spar type. It is very fit for the determination of the scattering power F of the light oxygen particle as the structure contains no parameter crystallographically undetermined and the effect of the light atoms is not dominated here by heavy ones [1]). The fact that the scattering power of Lithium is found at the same time, has two more advantages.

First it enables us to test the intensity formula [2]). When determining the scattering power a theoretical formula is used, which contains the reflecting power and some other factors changing according to the glancing-angle. In deducing the scattering power from the experimental intensities every error in the factors taken into account enters into the scattering power thus calculated [3]). If an ionic-lattice were assumed, we can expect the scattering power of lithium to fall off only slightly with increasing glancing-angle, the distances of the electrons from the nucleus being small. In interpreting the intensities we found this dependence to agree with the theoretical estimation; this is considered a proof of the intensity formula used. There are but few substances adapted for the testing of the powder-formula. In the case of light atoms the dependence of the scattering power, in that of heavy atoms the absorption in the rod causes great uncertainty [4]).

Secondly the simultaneous determination of F_{Li} has the advantage of giving a measure for the absolute value of the scattering power of oxygen

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[1]) J. M. BIJVOET and A. KARSSEN. Rec. Trav. Chim. **43**, 680 (1924).

[2]) *(Note added September 1926).* Lately this test was performed by comparing the powder intensities of NaCl with the well known measurements on the BRAGG-method. The powder intensities were measured ionometrically by R. J. HAVIGHURST (Proc. Nat. Acad. Sc. **12**, 375 1926), photographic measurements being made by L. HARRIS, S. J. BATES and D. A. MAC INNES (Phys. Rev. **28**, 235 1926). The powder-formula was found to hold good. Also c.f. A. H. COMPTON and N. L. FREEWAN, Nature **110**, 38 (1922).

[3]) J. M. BIJVOET, Werken van het Genootschap ter bev. van nat. genees- en heelkunde, XI, 512 (1926).

[4]) We are investigating whether in the case of a heavy powder the intensities of a rotating rod agree with the calculated intensities, assuming that the substance be homogeneously distributed over the surface. This is essential for the question to which degree quantitative measurements may be used in ordinary structure determinations.

(i. e. the ratio of the amplitude diffracted by the particle to that diffracted by a free electron). In general extrapolation of scattering powers as far as $\vartheta = 0$ is very uncertain because of their strong angle-dependence; for the *Li*-ion this extrapolation was possible, the dependence being found to be much smaller in this case. Putting $F_{Li^+_{\vartheta=0}} = 2$, F_O can be expressed in these units [1]).

2. The intensity formula reads

$$I = \int I_\vartheta \, d\vartheta \sim \frac{1 + \cos^2 \vartheta}{\sin^2 {}^\vartheta/_2 \cos {}^\vartheta/_2} \nu S^2 \; ^{2)}$$

Here I_ϑ is the intensity for diffraction-angle ϑ; the integration extends over the small domain in which reflection takes place. ν is the plane-number-factor, S the structure factor.

$\int I_\vartheta \, d\vartheta$ was measured photographically.

In general a factor must be added, which gives the influence of absorption in the rod. In our case — thin celluloid cylinders filled with loose powder of Li_2O, diameter 0.4—0.8 mm — calculation shows this factor to be constant within a few percents [3]). This, together with the accuracy of our measurements, permits to neglect the absorption. For the present the influence of the heat-motion is taken up in the *F*'s.

The sample being very finely powdered the extinction may be neglected [4]). This important advantage over the one-crystal method causes the examination of the applicability of the powder-method to quantitative measurements.

3. *Photographic intensity-measurements.*

The powder films were made with the apparatus described altero loco [5]). $Cu_{K\alpha}$ radiation was used, sometimes the β-radiation was filtered out by a *Ni*-filter.

The blackening of the photographic plate by homogeneous *X* rays was found proportional to the incident radiation if the blackening is less than 0.6 [6]). The blackening was measured with the fotometer of MOLL.

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[1]) We are investigating whether the powder method may give the absolute values of the scattering power from photograms of the substance in known mixture with a substance measured absolutely (e. g. NaCl).

[2]) P. DEBYE and P. SCHERRER. Phys. Zs. **19**, 474 (1918).
J. M. BIJVOET. Rec. Trav. Chim. **42**, 886 and 898 (1924).

[3]) A. CLAASSEN, Dissertation, Amsterdam 1926.

[4]) C. G. DARWIN. Phil. Mag. **43**, 800 (1922).
W. L. BRAGG, C. G. DARWIN and R. JAMES, Phil. Mag. (7) **1**, 897 (1926).

[5]) J. M. BIJVOET and A. KARSSEN. l.c.

[6]) P. P. KOCH. Ann. de Phys. **45**, 392 (1924).
R. GLOCKER and W. TRAUB. Phys. Zs. **22**, 345 (1921).
A. BROUWERS. Z. f. Phys. **14**, 374 (1923).
R. BLUNCK. Ann. d. Phys. **77**, 477 (1925).

The registered deviations of the galvanometer were transposed in terms of the blackening S, the quantity $\int S\, d\vartheta$ found by measuring the concerning area of the S-curve. In this way I of the intensity equation was found, S being proportional to I_ϑ.

4. *Accuracy of the measurements.*

The fainter lines were measured on long exposed films, the lines 111 and 220 on shorter exposed ones. The photograms reproduced — of half size, transmission X-ray film to photogram 1 : 10 — are examples of two of these film-parts; on a few films all the lines were well measurable.

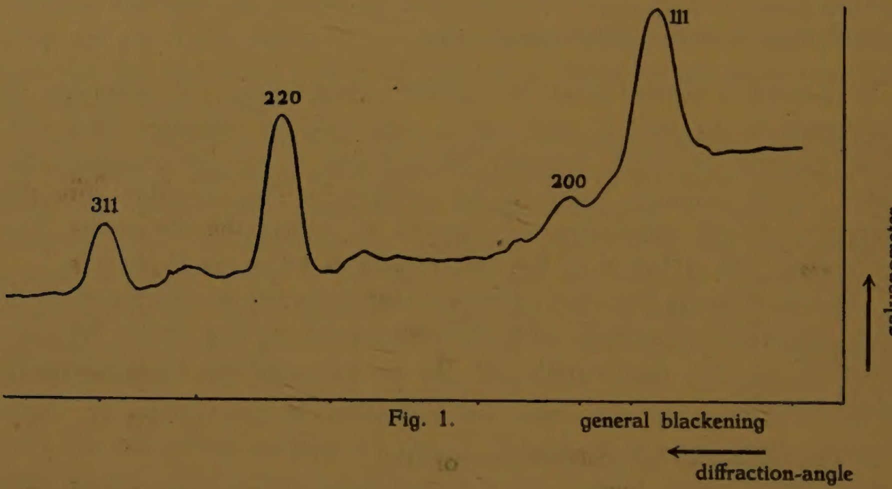

Fig. 1.

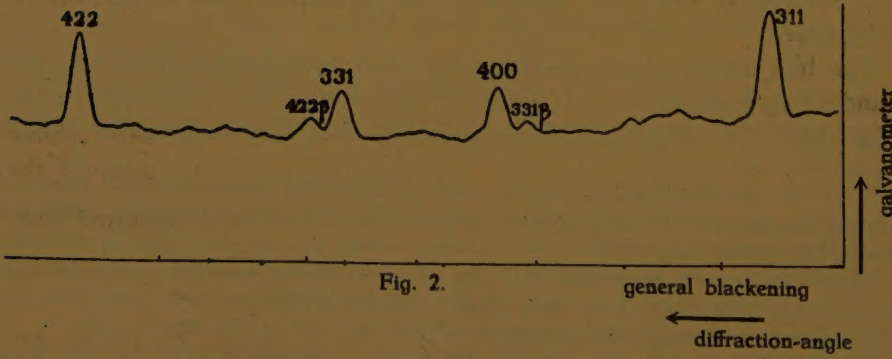

Fig. 2.

The average intensities of column 5 of table I were deduced from the photograms of the right and left halves of some ten films. The extreme values in column 5 show the reproducibility of the measurements. This is better than we expected. For 111 the discrepancies are large; this might have been caused by the great general blackening round this line or perhaps by its coincidence with the strongest diffraction line of *LiOH*. Li_2O being hygroscopic the hydroxide might have been formed in some small quantities in preparing the rod. The other diffraction lines of *LiOH* being absent, only very small quantities of *LiOH* must have been formed; no other *LiOH*-lines coincide with Li_2O lines but 111.

TABLE I.

1	2	3	4	5		6
$h_1\,h_2\,h_3$	S	$\sin \vartheta/_2$	A	I		S
				average	extreme values	
111	O	0.290	168	165	145—185	9.9
200	$O - 2\,Li$	0.334	91	± 13		± 3.8
220	$O + 2\,Li$	0.472	80	100		11.2
311	O	0.555	108	34	33— 35	5.6
400	$O + 2\,Li$	0.669	18	14	13— 15	8.8
331	O	0.729	66	14	12— 15	4.6
422	$O + 2\,Li$	0.819	70	30	29— 31	6.6
333 511	O	0.870	109	16	16— 17	3.8

Of the reflections with structure factor $2\,Li—O$ the line 200 was the only one which could be measured on a few films.

For most reflections the accuracy in S may be estimated at a few percents, as a great number of films was measured and the relative error in S amounts to half that in I ($S \sim \sqrt{I}$).

§ 5. *Calculation of the scattering powers.*

In table I column 1 contains the indices of the reflecting planes, column 2 the structure factor, column 3 the values of $\sin \vartheta/_2$, column 4 the values of $\nu \dfrac{1+\cos^2 \vartheta}{\sin^2 \vartheta/_2 \cos \vartheta/_2} = A$, column 5 the intensities I measured photographically, column 6 values proportional to $\sqrt{I/A}$ or S. In fig. 3 the values of S are plotted against $\sin \vartheta/_{2_{Cu}}$.

Then from the curves F_O and $2\,F_{Li} + F_O$ that for F_{Li} is deduced. The extrapolated part is dotted in the fig. [1].

In fig. 4 the curves for F_O and F_{Li} are reproduced once more, and here the value 2 is assigned to the ordinate of the intersection of latter curve with the axis.

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[1] This extrapolation assumes ions (see 6).

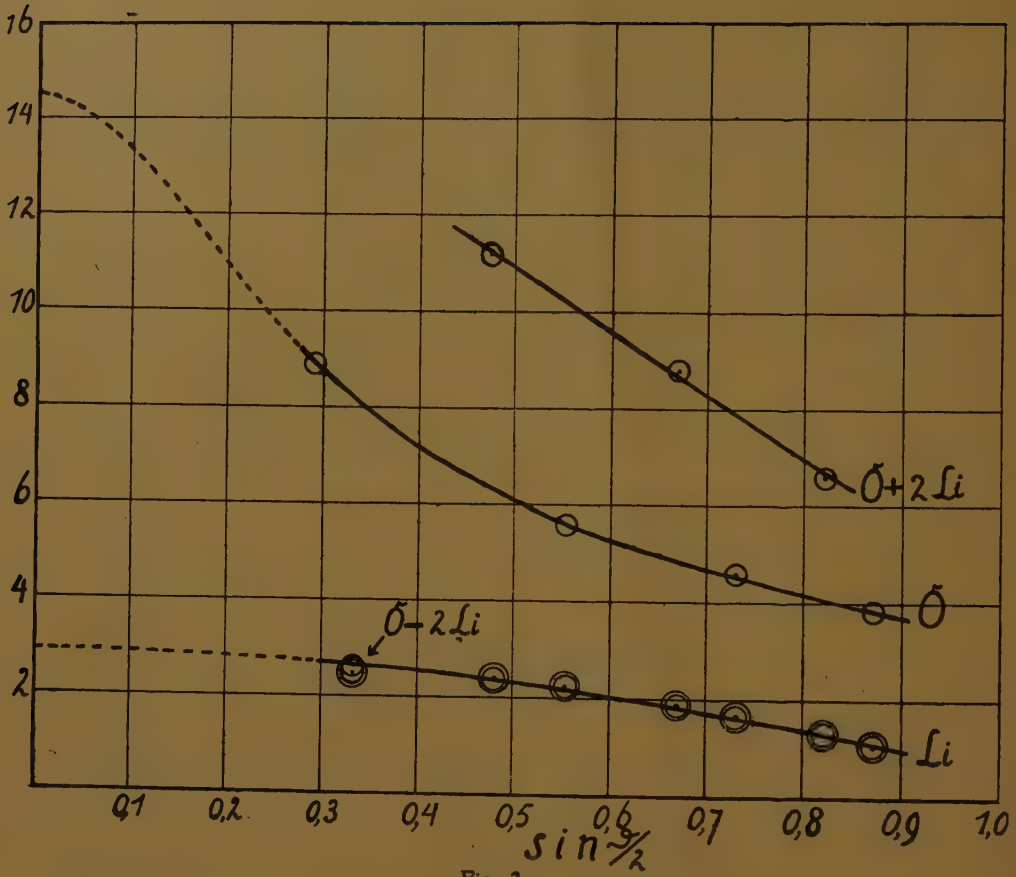
16
14
12
10
8
6
4
2
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1,0
sin ϑ/2
Ō+2Li
Ō
Ō−2Li
Li

Fig. 3.

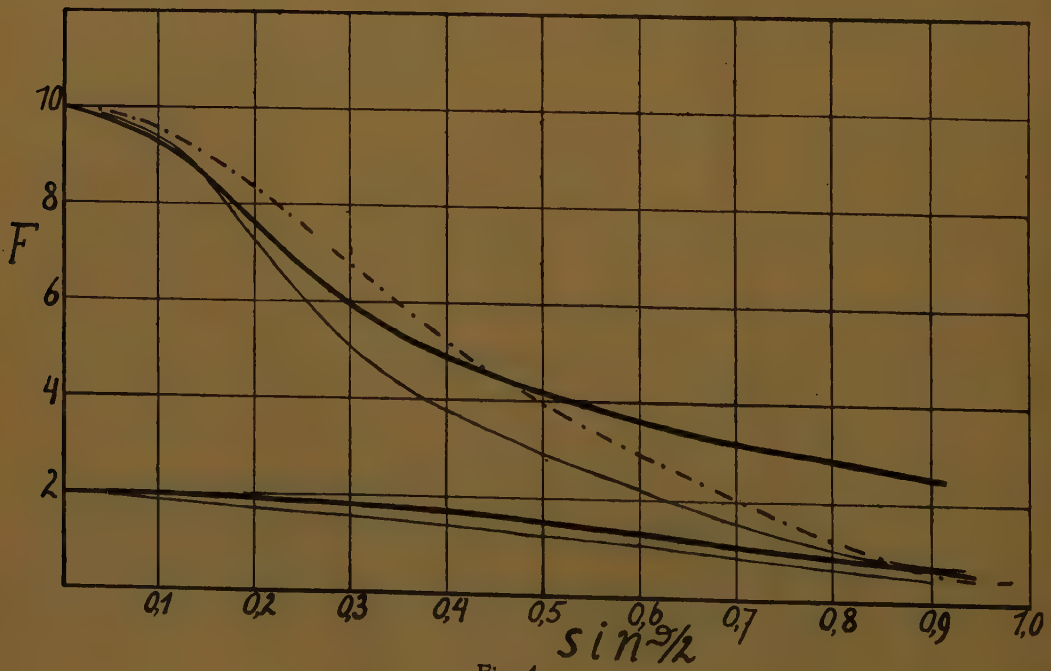
10
8
F
6
4
2
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1,0
sin ϑ/2

Fig. 4.

Table II gives some values of the scattering power of lithium and oxygen taken from fig. 4.

TABLE II.

$Sin\ \vartheta/2$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
F_{Li}	2	1.9^{5}	1.9	1.8	1.7	1.5	1.3	1.1	0.9	0.7
F_O	10	9.3	7.6	6.0	4.9	4.2	3.7	3.2	2.9	2.6

6. *Discussions of the scattering power of lithium and oxygen.*

As stated above the slight angle-dependence we found in the case of F_{Li} confirms the intensity formula used.

The non-extrapolated part of the F curve of oxygen shows the following features:

1. The decline is so great as to make the assumption of constant scattering power in crystal analysis quite impermittable for light atoms [1]).

2. The decline is much smaller than the one calculated for this domain by HARTREE, notwithstanding our *F*-values contain the temperature factor too. HARTREE's theoretical values, converted into *Cu*-radiation, give 3,3 : 0,9 for the ratio $Fo_{311} : Fo_{333}$; we found 3,9 : 2,7. On our basis of calculation the ratio $\frac{I_{311}}{I_{\substack{333\\511}}}$ should have been found some six times greater to get HARTREE's decline. Even without quantitave measurements this must undoubtedly be rejected.

Extrapolation of the F-curve is possible without great inaccuracy in the case of lithium if ions be assumed. Then a decline as given in the figure is the only one possible. This corresponds with the calculated dependence if the distance of both electrons to the nucleus be about one half the radius of the one-quantum-orbit of hydrogen. This result seems to be plausible; more accurate calculation is not possible without surpassing the accuracy of the measurements, which also contain the effect of the heat motion. It appears fully possible that the *Fo* curve will end for $\vartheta = 0$ at $F = 10$.

In Fig. 4 the — . — . — line represents HARTREE's calculated values. As stated above, for $sin\ \vartheta/_2 > 0{,}4$ our decline is much smaller than the one calculated.

Should an atomic lattice be assumed, than the *X*-ray data do not seem to be able to reject this assumption with certainty. [2])

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[1]) N. H. KOLKMEYER, J. M. BIJVOET and A. KARSSEN. Z. f. Phys. **20**, 82 (1923).

[2]) In our case one can easily ascertain that this is true. In the well-known example of *Li F* (P. DEBIJE and P. SCHERRER. Phys. Zs. **19**, 474 (1918)) too the deduction of ions being present is by no means conclusive.

7. *Comparison with other results.*

F-values for lithium can be derived from the photometrical data of DEBIJE and SCHERRER on *LiF*. The data of their Table III l.c. give a decline about equal to ours; their values are represented in Fig. 4 by a thin line.

On oxygen one of us made absolute measurements with Fe_3O_4 (magnetite) in the laboratory of Prof. W. L. BRAGG [1]. A decline was found still greater than that calculated by HARTREE. In Fig. 4 this decline is given by the thin line. The difference between both experimental curves seems to indicate that the scattering power of a particle is strongly dependent on its environment. For the oxygen ion with its relatively great number of outer electrons this is not astonishing.

8. We intend to continue our measurements with different wavelengths, at low temperature, on some analogous compounds and mixtures of known composition.

9. *Summary.* The scattering power *F* of lithium and oxygen is determined by photographic intensity measurements on Li_2O powder with $Cu_{K\alpha}$ rays.

F_{Li} was found to agree with the results of DEBIJE and SCHERRER on *LiF*. In the observed region *Fo* appeared to be much less dependent on the diffraction-angle as found by CLAASSEN in Fe_3O_4; the calculated values of HARTREE for a free oxygen-ion lie between both sets.

We wish to express our hearty thanks to our amanuensis Mr. A. KREUGER for his aid in the experimental part of this investigation.

We are much indebted to Prof. SMITS for his kind interest.

Lab. of General and Inorganic Chemistry
Amsterdam, July 1926. *of the University.*

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[1] A. CLAASSEN. Proc. Phys. Soc. London August 1926.

Chemistry. — *"Equilibria in systems, in which phases, separated by a semipermeable membrane"*. XVIII. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of November 27, 1926).

Influence of the pressure on osmotic systems.

We take a system E_P (of one or more phases) under the pressure P. We bring this system, while its temperature and total composition remain constant, under the pressure $P+dP$. Then a new system E'_{P+dP} arises, in which the phases can differ a little in composition with those of the first system; this difference in composition is defined by the value of dP.

In order to compare the $O.W.A.$ of the two systems:

$$E_P \qquad\qquad E'_{P+dP}$$

we represent the total thermodynamical potential of the first system by Z and that of the second system by Z'. We then have:

$$Z' = Z + VdP \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which V represents the total volume of system E under the pressure P. The $O.W.A.$ of the first system is defined by:

$$\varphi = \frac{\partial Z}{\partial w} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

if viz. $\frac{\partial Z}{\partial w} \cdot \delta w$ represents the change of the thermodynamical potential, which the first system receives, if this takes in δw quantities of water. The $O.W.A.$ of the second system now is:

$$\varphi' = \frac{\partial Z'}{\partial w} = \frac{\partial Z}{\partial w} + \frac{\partial V}{\partial w} \cdot dP \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We now put:

$$\frac{\partial V}{\partial w} = \Delta V_E$$

Hence is apparent that $\Delta V_E . \delta w$ represents the change, which gets the total volume V of system E, if this takes in δw quantities of water. If we put further $\varphi' = \varphi + d\varphi$ then (3) passes into:

$$d\varphi = \Delta V_E . dP \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

by which the change of the $O.W.A.$ is defined. We can also deduce (4) at once from (2) by differentiating this with respect to P.

As φ and the *O.W.A.* of a system change in opposite direction, we shall substitute in the following φ by $-\xi$; then the ξ and the *O.W.A.* of a system change in the same direction; then they become viz. at the same time larger or smaller. Consequently we may write instead of (2) and (4)

$$\xi = -\varphi = -\frac{\partial Z}{\partial w} \; (5^a) \qquad d\xi = -d\varphi = -\Delta V_E \, . \, dP \; . \; . \; (5^b)$$

It follows from (5^b):

the *O.W.A.* of a system E becomes smaller on increase of pressure, if ΔV_E is positive, and larger if ΔV_E is negative.

If we indicate by an arrow the direction, in which the water diffuses, then we can express this in the following way:

$$\Delta V_E > 0 \qquad E_P \leftarrow\!\!\!\!\!\mid\; E_{P+\Delta P} \; . \; . \; . \; . \; . \; . \; (6^a)$$

$$\Delta V_E < 0 \qquad E_P \mid\!\!\!\!\!\rightarrow E_{P+\Delta P} \; . \; . \; . \; . \; . \; . \; (6^b)$$

in which E_P represents the system under the pressure P and $E_{P+\Delta P}$ this same system under the pressure $P + \Delta P$, and in which ΔP is positive.

If both the systems E_1 and E_2 have the same *O.W.A.* under the pressure P, then we have the osmotic equilibruim:

$$(E_1)_P \mid (E_2)_P \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (7^a)$$

If we raise the pressure to $P + dP$ then both systems will have no more the same *O.W.A.*; that of the left system will increase with:

$$d\xi_1 = -\Delta V_{E_1} \, . \, dP$$

and that of the right system with:

$$d\xi_2 = -\Delta V_{E_2} \, . \, dP$$

If we take $\Delta V_{E_1} > \Delta V_{E_2}$ then, on increase of pressure, the *O.W.A.* of the right system becomes greater than that of the left system; consequently water will diffuse from left to right. We can represent this by:

$$\Delta V_{E_1} > \Delta V_{E_2} \qquad (E_1)_{P+\Delta P} \mid\!\!\!\!\!\rightarrow (E_2)_{P+\Delta P} \; . \; . \; . \; . \; (7^b)$$

in which ΔP is positive. Consequently we may say:

if we increase the pressure of an osmotic equilibrium, then the water diffuses in such direction that contraction of volume occurs.

We can deduce also in another way the influence of a change in pressure on the *O.W.A.* of a system. In previous communications (f.i. in Comm. VI) we have seen a.o. that the *O.W.A.* of a system E:

in which one or more liquids occur, is equal to the *O.W.A.* of each of those liquids;

in which by taking in — or losing a little water a liquid arises, is equal to the $O.W.A.$ of this liquid;

in which by taking in — or losing water a phases-reaction occurs, is equal to the $O.W.A.$ of a liquid with which that system can be in equilibrium.

The same is true also for systems with a vapour or for those which can be in equilibrium with a vapour.

If we represent the composition of the liquid or vapour, abovementioned, by:

$$xX + yY + zZ + \ldots\ldots + (1-x-y-z\ldots)\,W. \quad . \quad . \quad . \qquad (8^a)$$

or f.i. by:

$$wW + xX + yY + \ldots\ldots + (1-w-x-y\ldots)\,Q \quad . \quad . \quad . \qquad (8^b)$$

in which X, Y etc. (except W) may be components or composants, then the $O.W.A.$ of the system E is, therefore, defined by:

$$\xi = -\varphi = -\zeta + x\frac{\partial\zeta}{\partial x} + y\frac{\partial\zeta}{\partial y} + \ldots \quad . \quad . \quad . \quad . \quad . \qquad (9^a)$$

$$\xi = -\varphi = -\zeta - (1-w)\frac{\partial\zeta}{\partial w} + x\frac{\partial\zeta}{\partial x} + y\frac{\partial\zeta}{\partial y} \quad . \quad . \quad . \quad . \qquad (9^b)$$

If we bring the system E from the pressure P to $P + dP$ then the $O.W.A.$ of this system changes with:

$$d\xi = \frac{\partial\xi}{\partial P}\,.\,dP + \frac{\partial\xi}{\partial x}\,.\,dx + \frac{\partial\xi}{\partial y}\,.\,dy + \ldots \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

It now depends on the number of freedoms of the system E whether $dx\,dy$ etc. are completely defined by the change in pressure dP; if this is not the case, then we can put still different conditions, which must be satisfied by the changes of the system.

In order to apply those general considerations to some simple cases, we take the systems:

$$E = G \; (11^a) \qquad E = L \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11^b)$$

which consist each of one phase only; the change of the $O.W.A.$ at a change of pressure is defined by (5^b). For system (11^a) $\triangle V_E\,.\,\delta w$ now represents the increase of volume, which gets one quantity of vapour, if this takes in δw quantities of water; for system (11^b) it is the increase of volume if one quantity of liquid takes in δw quantities of water. This increase of volume is positive for vapours and also in general for liquids, excepted in the special case that the contraction occurring with the mixture would be still greater than the volume of the taken δw quantities of water. In the following, unless the opposite is precisely said, we shall take this increase of volume positive. We then find:

the *O.W.A.* of a vapour and that of a liquid becomes smaller on increase of pressure and larger on decrease of pressure.

In the osmotic systems:

$$G_P \mathrel{\vert\!\!\!\leftarrow} G_{P+\Delta P} \, (12^a) \qquad L_P \mathrel{\vert\!\!\!\leftarrow} L_{P+\Delta P} \, . \quad . \quad . \quad . \quad . \quad (12^b)$$

the water diffuses, therefore, in the direction of the arrows [compare also system (6^a)].

In order to express the change in volume ΔV_E, mentioned above, we take a vapour G or liquid L of the composition:

$$x \, Mol \, X + y \, Mol \, Y + (1 - x - y) \, Mol \, W \quad . \quad . \quad . \quad . \quad (13)$$

with the volume V. If we mix this with δw quantities of water, then arise $1 + \delta w$ quantities of a new vapour or liquid, which differs infinitely little (dx and dy) in composition from the original. Consequently we have:

$$\Delta V_E \, . \, \delta w = (1 + \delta w) \left(V + x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} \right) - V . \quad . \quad . \quad (14)$$

For dx and dy we find:

$$dx = \frac{x}{1 + \delta w} - x = \frac{-x \, . \, \delta w}{1 + \delta w} \qquad dy = \frac{y}{1 + \delta w} - y = \frac{-y \, . \, \delta w}{1 + \delta w} \, . \quad (15)$$

If we substitute those values in (14), then follows:

$$\Delta V_E = V - x \frac{\partial V}{\partial x} - y \frac{\partial V}{\partial y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

the second part of which in the case of a vapour, which follows the gas-laws, passes into the volume V of that vapour.

We are able to deduce this also in the following way. The *O.W.A.* of a vapour or liquid (13) is defined by:

$$\xi = - \varphi = - \zeta + x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Hence follows, in connection with the value of ΔV_E from (16):

$$d\xi = - \Delta V_E \, dP + (rx + sy) \, dx + (sx + ty) \, dy \quad . \quad . \quad . \quad (18)$$

If we keep constant the composition of this vapour or liquid, so that dx and dy are zero, then (18) passes into (5^b).

As we can give still arbitrary values to dx and dy in (18), we choose them in such a way, that the new system E' arises from E by taking in or losing a little water. We then have to put:

$$dx : x = dy : y = d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

so that $d\lambda$ is positive if the liquid or vapour loses water. With the aid of (19) now (18) passes into:

$$d\xi = - V_E \, dP + (rx^2 + 2 \, sxy + ty^2) \, d\lambda \quad . \quad . \quad . \quad . \quad (20)$$

We define the system E' in such a way that its $O.W.A.$ under the pressure $P + dP$ is equal to that of system E under the pressure P. As then $d\xi$ must be zero, follows from (20)

$$d\lambda = \frac{V_E}{rx^2 + 2\,sxy + ty^2}\,dP \quad \ldots \ldots \quad (21)$$

in which the denominator, as long as we consider stable states, is positive. As, therefore, $d\lambda$ and dP have the same sign, it follows:

if we increase the pressure of a liquid or vapour with a definite amount dP, then this must lose a definite quantity of water, in order to keep the same $O.W.A.$

We take a liquid c of fig. 1 under the pressure P; all liquids, which have under this same pressure the same $O.W.A.$ as this liquid L_c are situated on the isotonic curve acb going through point c. If we take the same liquid L_c under a pressure $P + dP$, then all liquids which have the same $O.W.A.$ under this pressure $P + dP$ as L_c, will be situated also on an isotonic curve a_1cb_1 going through point c, which curve, as follows from the previous considerations, does not coincide with acb.

If we take viz. an arbitrary liquid q of curve acb, then this is isotonic with L_c under the pressure P; consequently we have the osmotic equilibrium:

$$(L_c)_P \mid (L_q)_P \quad \ldots \ldots \ldots \quad (22)$$

If we represent the increase of volume of the liquids L_c and L_q when taking in δw quantities of water, by $\triangle V_c \,.\, \delta w$ and $\triangle V_q \,.\, \delta w$, then, if we bring the pressure of (22) to $P + dP$, the $O.W.A.$ of the left system increases with $-\triangle V_c \,.\, dP$ and that of the right system with $-\triangle V_q \,.\, dP$. As $\triangle V_c$ and $\triangle V_q$ are different in general, L_c and L_q are no more isotonic, therefore, under the pressure $P + dP$. The isotonic curve of the pressure $P + dP$ which goes through the point c must be therefore, an other than that of the pressure P.

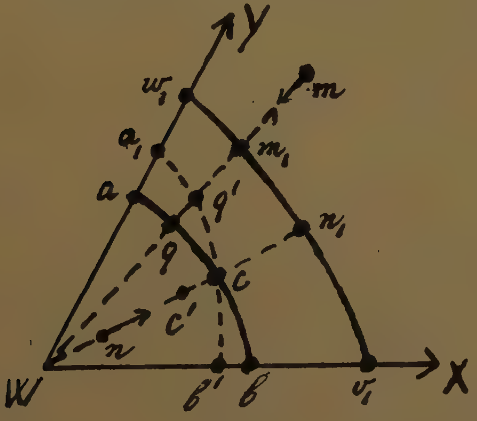

Fig. 1.

We are able to show this also in the following way. For the osmotic equilibrium (22) is true:

$$\left(\zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y}\right)_c = \left(\zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y}\right)_q \quad \ldots \quad (23)$$

For an osmotic equilibrium:

$$(L_c)_{P+dP} \mid (L'_q)_{P+dP} \quad \ldots \ldots \ldots \quad (24)$$

in which L'_q represents a liquid, which differs infinitely little (dx and dy) from L_q then follows from (23):

$$\triangle V_c \, . \, dP = \triangle V_q \, . \, dP - (rx + sy)_q \, dx - (sx + ty)_q \, dy \quad . \quad . \quad (25)$$

If we choose L'_q in such a way that it is represented by a point q' (fig. 1) on the line Wq then dx and dy satisfy (19); (25) now passes into:

$$(rx^2 + 2\,sxy + ty^2)_q \, d\lambda = (\triangle V_q - \triangle V_c) \, . \, dP \quad . \quad . \quad . \quad (26)$$

$(\triangle V_q - \triangle V_c)\,\delta w$ is the change in volume if δw quantities of water diffuse from L_c towards L_q. As in general this change is not zero, $d\lambda$, therefore, has a value, different from zero. If $d\lambda$ is positive, then point q' is situated as is drawn in fig. 1.

If L_q proceeds along the curve acb, then the value of $\triangle V_q - \triangle V_c$ changes; if q coincides with c, then this value is zero of course. If we take this value positive, if q is situated between a and c and negative if q is situated between c and b, then we can represent the isotonic curve of the pressure $P + dP$ $(dP > 0)$ by $a_1\,c\,b_1$. For small values of dP those curves $a\,c\,b$ and $a_1\,c\,b_1$ have the same direction with approximation in the point c.

Above we have seen that both the liquids of (22) are no more in equilibrium with one another under a pressure $P + \triangle P$. If we keep constant the total composition, then, as we have deduced already above in general for system (7^a) in (7^b), the water will diffuse under the pressure $P + \triangle P$ in such direction that the total volume decreases. If we take $\triangle V_q > \triangle V_c$ then a little water must diffuse, therefore, from L_q towards L_c; we shall represent this, just as in (7^b) by:

$$\triangle V_q > \triangle V_c \qquad (L_c)_{P+\triangle P} \leftarrow\!\!\!\!\!| \;\; (L_q)_{P+\triangle P} \quad . \quad . \quad . \quad . \quad (27)$$

Under the pressure $P + \triangle P$ a new osmotic equilibrium:

$$(L'_c)_{P+\triangle P} \;\vdots\; (L'_q)_{P+\triangle P} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

is formed, therefore.

If we represent the liquids of this latter osmotic equilibrium in fig. 1 by c' and q', then the line $q'\,c'$ must go through the point (situated on the line $c\,q$) which represents the complex of the liquids L_q and L_c. The position of the points q' and c' depends, therefore, not only on the value of dP, but also on the ratio of the quantities of the two liquids. We can deduce this also as follows.

For the osmotic equilibrium (22) equation (23) is valid; for an osmotic equilibrium (28), of which pressure and composition of the liquids differ a little from (22) then is valid:

$$\left.\begin{aligned} &\triangle V_c \, . \, dP - (rx + sy)_c \, . \, dx_c - (sx + ty)_c \, . \, dy_c = \\ &\quad = \triangle V_q \, . \, dP - (rx + sy)_q \, . \, dx_q - (sx + ty)_q \, . \, dy_q \end{aligned}\right\} \quad . \quad . \quad (29)$$

In our case we have to define in such a way the changes of the concentrations: dx_c etc., that L'_c arises from L_c by taking in δw quantities of water and L'_q from L_q by giving δw quantities of water (δw positive or negative). If there are n quantities of L_c and m quantities of L_q then we find:

$$\left.\begin{array}{ll} dx_c = -\dfrac{x_c}{n}\,.\,\delta w & dy_c = -\dfrac{y_c}{n}\,.\,\delta w \\ dx_q = +\dfrac{x_q}{m}\,.\,\delta w & dy_q = +\dfrac{y_q}{m}\,.\,\delta w \end{array}\right\} \quad . \quad . \quad . \quad . \quad (30)$$

If we substitute those values in (29) and if we put:

$$(x^2 r + 2\,xys + y^2\,t)_c = K_c \qquad (x^2 r + 2\,xys + y^2\,t)_q = K_q$$

then follows:

$$\left(\frac{K_c}{n} + \frac{K_q}{m}\right)\delta w = (\triangle V_q - \triangle V_c)\,dP \quad . \quad . \quad . \quad . \quad . \quad (31)$$

so that δw has the same sign as dP. In accordance with (27) we find, therefore, that for positive values of dP the water diffuses from L_q towards L_c, (31) defines, however, also δw and in accordance with (30), therefore, also dx_c etc., as function of the quantities n and m of both the liquids.

If we take infinitely large the quantity of L_c in (22) then its composition rests unchanged when taking in δw quantities of water; equilibrium (28) then is the same as (24). As n becomes infinitely large, $K_c : n$ in (31) becomes zero, therefore, and as $\delta w : m$ in (31) is equal to $d\lambda$ in (26), then (31) passes into (26).

In the osmotic equilibrium

$$(W)_P \,\vdots\, (L_1)_{P_1} \quad \text{(fig. 1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

we find at the left side of the membrane pure water under the pressure P and at the right side of the membrane a liquid L_1 under the pressure P_1. In this special case, therefore, $\pi = P_1 - P$ is the osmotic pressure of the liquid L. The osmotic equilibrium (32) is defined by:

$$(\zeta_W)_P = \left(\zeta_1 - x_1\frac{\partial \zeta_1}{\partial x_1} - y_1\frac{\partial \zeta_1}{\partial y_1}\right)_{P_1} \quad . \quad . \quad . \quad . \quad . \quad (33)$$

If we consider stable states only: then we can show in a similar way as f.i. in communication I that (33) can be satisfied only if $P_1 > P$. We now give a definite value to both pressures; then it follows from (33) that the liquids L_1 of (32) are represented by a curve, f. i. curve $w_1\,v_1$ in fig. 1.

As under this pressure P_1 all liquids of the region $Ww_1\,v_1$ have a smaller $O.W.A.$ than the liquids of curve $w_1\,v_1$ under this same pressure P_1 and as those of the region $w_1\,v_1\,XY$ have a greater $O.W.A$ than the liquids of curve $v_1 w_1$, it follows, therefore:

under a pressure $P_1 > P$ all liquids
of curve $w_1\,v_1$ have the same,
of region $Ww_1\,v_1$ have a smaller,
and of region $w_1\,v_1\,XY$ have a greater,
$O.W.A.$ than that of pure water under the pressure P.

If we take, therefore, the osmotic systems:

$$(W)_P \overset{|}{\underset{|}{\rightarrow}} (L_m)_{P_1} \qquad (W)_P \overset{|}{\underset{|}{\leftarrow}} (L_n)_{P_1} \quad \text{(fig. 1)} \; . \; . \; . \; . \; . \quad (34)$$

then in the first system the water diffuses from the pure water towards the liquid; in the second system, however, water diffuses from the liquid towards the pure water; the liquids m and n move in fig. 1, therefore. in the direction of the arrows, till they reach curve $w_1\, v_1$ (if in the first of those systems a sufficient quantity of pure water is present). Then the systems (34) pass into the osmotic equilibria:

$$(W)_P \;\vdots\; (L_{m_1})_{P_1} \qquad (W)_P \;\vdots\; (L_{n_1})_{P_1} \quad \text{(fig. 1)} \; . \; . \; . \; . \; . \quad (35)$$

We now take in fig. 2, in which $w_1\, v_1$ represents the corresponding curve of fig. 1, a liquid L of curve $a b$. If $a b$ is an isotonic curve of the pressure P, then all liquids of this curve $a b$ have the same $O.W.A.$ under the pressure P. If we replace in (32) the pure water by this liquid L, then an osmotic equilibrium:

$$(L)_P \;\vdots\; (L_1)_{P_1} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (36)$$

arises, in which of course the liquids L_1 now must have an other composition than in (32). As the $O.W.A.$ of the liquids of curve $a b$ under the pressure P is greater than that of the pure water under this same pressure, curve $a_1\, b_1$ which represents the liquids L_1 of (36) must be situated in fig. 2 further from the point W than curve $w_1\, v_1$.

Every arbitrary liquid L of curve $a b$ has, therefore, under the pressure

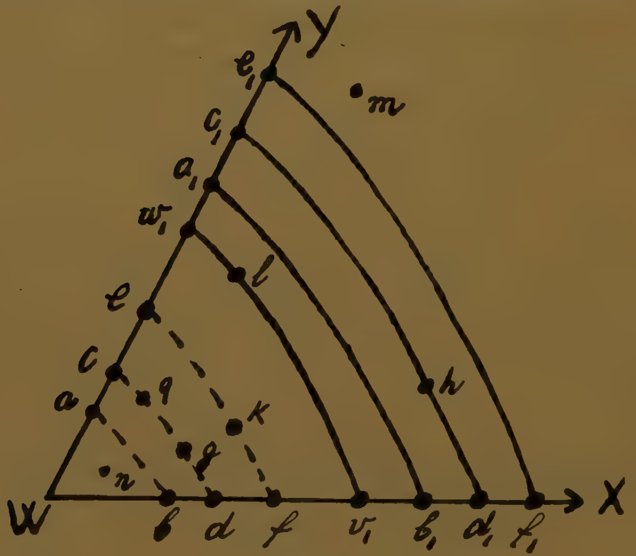

Fig. 2.

P the same $O.W.A.$ as every arbitrary liquid of curve $a_1\, b_1$ under the pressure P_1; we may call those curves $a b$ and $a_1\, b_1$ conjugated isotonic curves of the pressures P and P_1. The same is true for the curves $c d$

and $c_1 d_1$, for ef and $e_1 f_1$ etc. Consequently we find in fig. 2 a.o. the osmotic equilibria:

$$(W)_P \mid (L_l)_{P_1} \qquad (L_a)_P \mid (L_{a_1})_{P_1} \qquad (L_a)_P \mid (L_{b_1})_{P_1}$$

$$(L_g)_P \mid (L_h)_{P_1} \qquad (L_q)_P \mid (L_{d_1})_{P_1} \qquad (L_k)_P \mid (L_{f_1})_{P_1}$$

If we consider two conjugated isotonic curves of the pressures P and P_1 f.i. the curves cd and $c_1 d_1$ then follows from this:

under a pressure $P_1 > P$ all liquids
of the isotonic curve $c_1 d_1$ have the same
of the region $Wc_1 d_1$ have a smaller
and of the region $c_1 d_1 XY$ have a greater
$O.W.A.$ than the liquids of curve cd under the pressure P.

Hence follows that in the osmotic system:

$$(L_g)_P \rightarrow (L_m)_{P_1} \quad \text{(fig. 2)} \quad \ldots\ldots\ldots \quad (37)$$

the water must diffuse from left to right. It now depends on the ratio of the quantities of both liquids on which conjugated isotonic curves the equilibrium will be formed. If this is the case f.i. on the curves ef and $e_1 f_1$ then is formed the osmotic equilibrium:

$$(L'_g)_P \mid (L'_m)_{P_1} \quad \text{(fig. 2)} \quad \ldots\ldots\ldots \quad (38)$$

in which the left liquid in fig. 2 is represented by the point of intersection of the line Wg with curve ef and the right liquid by the point of intersection of Wm with $e_1 f_1$.

This conversion of (37) into (38) is possible, of course, only then, when the complex of the liquids L_g and L_m is situated within the region eff_1e_1; if this is not the case, then the system (37) also can not be formed on the curves ef and $e_1 f_1$.

We now take the osmotic systems:

$$\left.\begin{array}{ll} (L_g)_P \mid (L_g)_P & (L_g)_P \mid (L_q)_P \\ (L_g)_P \rightarrow (L_l)_P & (L_g)_P \leftarrow (L_n)_P \end{array}\right\} \quad \text{(fig. 2)} \quad \ldots\ldots \quad (39)$$

in which in all at the left side of the membrane the liquid L_g is present; the pressure is equal on both sides of the membrane, viz. P. It appears from fig. 2 that both the first systems then form osmotic equilibria, in the third system the water diffuses towards the right and in the last system towards the left.

If, however, we bring at the right side of the membrane the pressure from P to P_1 then all liquids, at the right side of the membrane are situated within the region $Wc_1 d_1$ of fig. 2; consequently they have all a smaller $O.W.A.$ than the liquid L_g under the pressure P. Instead of (39) we then get the systems:

$$\left.\begin{array}{ll} (L_g)_P \leftarrow (L_g)_{P_1} & (L_g)_P \leftarrow (L_q)_{P_1} \\ (L_g)_P \leftarrow (L_l)_{P_1} & (L_g)_P \leftarrow (L_n)_{P_1} \end{array}\right\} \quad \text{(fig. 2)} \quad \ldots\ldots \quad (40)$$

in which the water diffuses towards the left. If the ratio of the quantities of both liquids in each of those systems is chosen in such a way, that the equilibrium is formed on the conjugated isotonic curves ab and a_1b_1, then the left liquid is represented by the point of intersection of the line Wg with curve ab; the right liquids are represented by the points of intersection of the lines Wg, Wq, Wl and Wn with curve a_1b_1.

We now take the osmotic equilibrium:

$$(G)_P \mid (G_1)_P \tag{41}$$

in which on both sides of the membrane a vapour under the pressure P. If we bring the pressure on both sides of the membrane to $P+\triangle P$, then [comp (7^a) and (7^b)] the water must diffuse in such direction, that the total volume decreases. If, however, those vapours, follow the gas-laws, then the total volume does not change at diffusion of water, consequently (41) passes, without diffusion occurs, into the osmotic equilibrium,

$$(G)_{P+\triangle P} \mid (G_1)_{P+\triangle P} \tag{42}$$

This appears still also as follows. In the previous communication we have seen that two vapours are in osmotic equilibrium, when the partial vapour-pressure of the water-vapour is equal in both. If this is the case under the pressure P then this is also the case under the pressure $P+\triangle P$; if (41) is an osmotic equilibrium, then (42) it is also, therefore.

At last we still consider the osmotic equilibrium:

$$G_P \mid L_P \tag{43}$$

We now imagine that fig. 1 (XVII) is valid for this pressure P; then the vapour G is represented by a point of the gas-branch and the liquid L by a point of the liquid-branch of an isotonic curve; if, therefore, G is represented by a point f.i. of curve hc then L is situated anywhere on curve c_1l_1.

We now bring the pressure of (43) to $P+\triangle P$ and we take $\triangle P$ positive; we then get the osmotic system:

$$G_{P+\triangle P} \mid\!\!\!\rightarrow L_{P+\triangle P} \tag{44}$$

in which both the phases have no more the same $O.W.A$. That of the left system decreases viz. with $\triangle V_G \,.\, \triangle P$ and that of the right system with $\triangle V_L \,.\, \triangle P$ and as in general we may assume that $\triangle V_G > \triangle V_L$, the right system has a greater $O.W.A.$ than the left, therefore. Consequently the water diffuses in (44) in the direction of the arrow. This follows also, when applying the rule, that the water on increase of pressure diffuses in such direction that the total volume decreases.

(To be continued).

Physics. — *"On the Maximum and Minimum Density and the Heat of Evaporation of Helium"*. (First Part). By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of September 25, 1926).

A. Theoretical Part.

1. Introduction.

It has become known through the investigations of KAMERLINGH ONNES (Comm. Leiden **119** (1911)), and later through those of KAMERLINGH ONNES and BOKS (Comm. **170**^{b} (1924)), that the liquid density of Helium shows a *maximum* at 2°,3 abs. The course sketched in this latter paper leads us, however, to expect that, at still lower temperature, another *minimum* will appear; accordingly after this D_1 will again increase up to the absolute zero (See Fig. 1). The following simple theoretical considerations really confirm this supposition. We see from the values, calculated in § 3, that the minimum (at 0°,52) is exceedingly flat, and that the liquid density between $T=0$ and somewhat more than 1° abs. varies only very little — quite conformable to the diagram given p. 23 of Comm. 170^b.

Presently it wil also appear theoretically, that the internal molecular heat of evaporation $\lambda = L - p(v_2 - v_1)$ does not only — like L itself — present a *maximum* at 3°,4 (that of L lies at 3°,5), but that at lower temperature λ also passes through a *minimum*, and this at 1°,47. It can easily be shown that L does *not* pass through a minimum, but has a *point of inflection* in the neighbourhood of 2°,3. (Cf. Fig. 2; the values given there are expressed in "normal" units; multiplication by 542,63 yields L and λ in gr. cal.). The experiments of KAMERLINGH ONNES and DANA

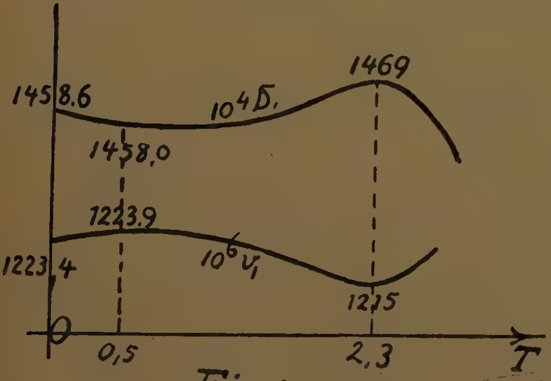

Fig. 1

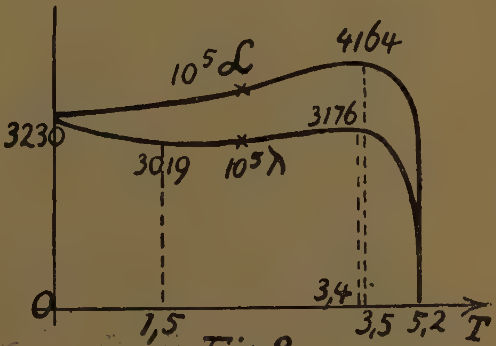

Fig. 2.

recently published (These Proc. **29**, 1051—1060 (1926)) only give the maximum of L at 3°,5, for which we theoretically calculate 22,6 gr. cal.; experimentally also 22,6 is found, but at about 3°. The experiments are, however, not accurate enough to determine this temperature with certainty; compare on this point the Second Part of this Article.

The course of both, that of Fig. 1 and Fig. 2 — and to this is added the low temperature coefficient of the *constant* of EÖTVÖS (cf. VAN URK, KEESOM and KAMERLINGH ONNES, ibid. **28**, 958 (1925)) and the too low values of the *specific heat* (DANA and KAMERLINGH ONNES, ibid. **29**, 1061—1068 (1926)), but this we will treat in a later paper — is only accounted for by the fact, that in Helium below T_k the quantity a does not diminish with increasing temperature, as in all other substances, but *increases*. As secondary factor we have then the in itself *small value* of a in Helium. The quantity b *always* decreases with increasing temperature (this decrease is not to be confused with the increase of b with the *volume*, which may, however, be neglected in Helium at the lower temperatures, since then v_1 remains *practically* unchanged); and this, like the decrease of a, in consequence of exponential temperature functions occurring by the side of a and b (BOLTZMANN's factors of distribution; c.f. among others "Zustandsgl.", p. 55-64). In all other substances the two decreases will counteract each other in the equation of state, and about neutralize each other, so that no special complications will appear, but in Helium the increase of a will act in the same direction as the decrease of b, and as we shall see, there the action of the two influences will give rise to the above-mentioned maxima and minima of D_1 and λ, in consequence of alternately stronger and weaker coöperation.

It need scarcely be stated, that in the fact of the relatively *too small* liquid density at low temperatures lies also the key to the phenomenon that Helium cannot become solid at the ordinary vapour pressures. Not until the *external* pressure is raised, through which the too small internal pressure a/v^2 (in consequence of the decrease of a at fall of temperature) is compensated, there can be question of solidification. Which has, indeed, proved to be true through KEESOM's recent experiments.[1]

That the phenomenon of the maximum density is a concequence of the decrease of a with falling temperature, I showed already in 1920 (Recueil Tr. Chim., **34**, 382), though at the time I still shared KAMERLINGH ONNES' (erroneous) view, that the liquid density could again diminish to a very small value at very low temperature, in other words might give rise to a second vapour phase. This would be the consequence of KAMERLINGH ONNES' assumption (Comm. **119** (1911); cf. particularly § 6, p. 15—19), that a would be $= cT^2$ (loc. cit. p. 17), in other words would become $=0$ at $T=0$. The later, above-mentioned investigations of KAMERLINGH ONNES and BOKS have contradicted these, in fact pretty improbable, assumption. We shall see in § 2 that $10^6\, a$, which quantity has the value of 67,4 at T_k, approaches to 39,5 at $T=0$, hence by no means $=0$. The assumption $a=cT^2$ would not be able to explain the minimum at 0°,5, nor that of λ at 1°,5. No more is the so-called „energy-degeneration" at lower temperatures, on which e.g. VERSCHAFFELT (see the cited paper by DANA and KAMERLINGH ONNES) refers, able to do so. I, therefore, disputed this view already in the paper of 1920 mentioned before (p. 382 under: "L'effet des "quanta" n'y est pour rien, etc."). Later on I worked out the theory on a better basis (L'Hydrogène et les gaz nobles, Leiden, Sijthoff, 1921, p. 39—41), and this theory is the same as will be developed in what follows (with only slight modification as regards db/dt).

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[1] Cf. on this subject my article in the N. Rott. Ct. of July 21th (Evening paper A. p. 1) and (without the numerous confusing printer's errors that occur in the N. R. Ct.) in the Journal de Genève of July 26th 1926. Cf. also Chem. Weekbl. of July 31st (under "Personalia").

Through my researches on the equation of state I have, of late, entirely relinquished the idea that in the case of *liquids* there could be question of "energy-degeneration", even at the lowest temperatures. ¹) Not only that all the phenomena of ordinary substances, and even the so greatly diverging ones of Helium can be explained qualitatively and quantitatively by the dependence of a and b on the temperature, and the dependence of b on the volume; this being *not* the case on assumption of energy-degeneration (the coefficient of expansion, inter alia, would simply rapidly approach to 0 without maximum nor minimum volume; the minimum for λ remained unexplained, etc.) — but in principle I protest against applying PLANCK's and DEBYE's considerations, which are especially valid for "oscillators" moving round fixed positions of equilibrium, to liquids (and even to gases!), where the molecules can move freely with regard to each other. Especially in Germany, where, in spite of all that has been written about it — even by VAN DER WAALS himself already — a and b are still almost universally considered as constant, physicists have recourse to the assumption of energy degeneration for liquids, in imitation of NERNST c. s. (vapour-pressure equations with $+1,75 \log T$, even at the highest temperatures, etc.).

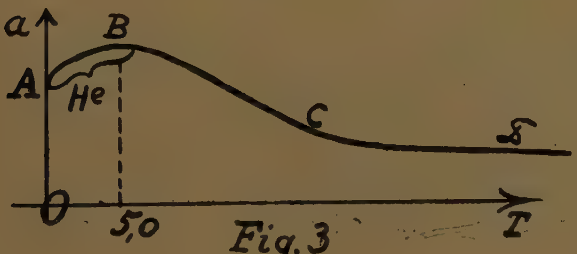

Fig. 3

With regard to this decrease of a in Helium at fall of temperature it may be pointed out, that this is a *quite general* phenomenon. There is (see Fig. 3) between B and D, i. e. almost over the total course of a,

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¹) PALACIOS MARTINEZ and KAMERLINGH ONNES (Comm. **164** (1923)) showed already for H_2 and He that — in contradiction to the opinion of some authors — there is not yet question of any quantum effect in the gaseous state at very low temperatures (20°,5 abs.).

a decrease with increasing temperature (see above: BOLTZMANN's distribution factor); only at *very* low temperatures there will be found decrease after a maximum on further fall of the temperature (Cf. on this point also my considerations in These Proc. **21**, 19 (1918)). As a is practically independent of v, the results found there for large volumes may also be applied to small volumes.

What is now the case? For almost all substances the region *between melting point and critical temperature* lies in the descending part, e. g. in the neighbourhood of C; only for hydrogen the part left of B is encroached on a little. Helium is, however, the only substance where the region between 0° and 5°,2 lies *almost entirely* between A and B. (The maximum lies at exactly 5°, so that T_k lies slightly on the right of B). Also for ordinary substances deviating phenomena would make their appearance at very low temperatures, but this is prevented by the appearance of the *solid* state long before the time.

2. The maximum of density at 2°,3. Formulae for a and b.

As $\left(\frac{dv}{dt}\right)_p = \left(\frac{dp}{dt}\right)_v : -\left(\frac{dp}{dv}\right)_t$, and the coefficient of compressibility $-\frac{1}{v}\left(\frac{dv}{dp}\right)_t$ always remains finite, hence never becomes 0 or ∞, $\left(\frac{dv}{dt}\right)_p$ will necessarily become 0 (maxima and minima of v) at the same time with $\left(\frac{dp}{dt}\right)_v$ or $T\left(\frac{dp}{dt}\right)_v$. From $p = \frac{RT}{v-b} - \frac{a}{v^2}$ follows:

$$T\left(\frac{dp}{dt}\right)_v = \frac{RT}{v-b} - \frac{Ta'}{v^2} + \frac{RT^2\,b'}{(v-b)^2} = \frac{a-Ta'}{v^2} + \frac{RT^2\,b'}{(v-b)^2} + p,$$

when for shortness a' is written for $\left(\frac{da}{dt}\right)_v$ and b' for $\left(\frac{db}{dt}\right)_v$.

If for the present — for the calculation of different quantities — we confine ourselves to the minimum of v at 2°,3, we shall have there:

$$a - Ta' = -\left(\frac{v}{v-b}\right)^2 RT^2\,b' - pv^2 \;(2°,3).$$

From the equation of state follows, however;

$$\frac{v}{v-b} = \frac{a/v + pv}{RT} = \frac{a/v}{RT}\left(1 + \frac{p}{a/v^2}\right),$$

so that we may also write:

$$a - Ta' = -\left(\frac{a^+}{v}\right)^2 \frac{b'}{R} - pv^2,$$

where, accordingly, a^+ means $a\,(1 + p : a/v^2)$. We shall see that for Helium at 2°,3 the different correction quantities may not be neglected.

Putting now

$$a = a_0 + \alpha T - \gamma T^2 \quad ; \quad b = b_0 - \beta T + \delta T^2,$$

we have the following equation at 2°,3, with $a - Ta' = a_0 + \gamma T^2$:

$$\underline{a_0 + \gamma T^2 = \left(\frac{a^+}{v}\right)^2 \frac{\beta - 2\,\delta T}{R} - {\scriptstyle pv^2}\ (2^\circ{,}3)} \quad . \quad . \quad . \quad . \quad (1)$$

This is already a *first* relation between a_0, α, γ and $-b' = \beta - 2\,\delta T$, when v is experimentally known.

A *second* relation is found from (for a is practically independent of v, and the above expression for a is, therefore, certainly valid up to T_k)

$$a_k = a_0 + \alpha T_k - \gamma T_k^2,$$

i.e. with $T_k = 5^\circ{,}19$ and $10^6\, a_k = 67{,}42$ (to be calculated from T_k and p_k)

$$\underline{a_0 + 5{,}19\,\alpha - 26{,}94\,\gamma = 67{,}42 . 10^{-6}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

A *third* relation follows from the theoretical value of the internal molecular heat of evaporation λ. For this, as the difference of two energies, the following equation is evidently valid — when, as we suppose, no energy degeneration occurs in liquids:

$$\lambda = \int_{v_1}^{v_2} \left(T \left(\frac{dp}{dt} \right)_v - p \right) dv,$$

which, accordingly, yields with the above-found value of $T\left(\frac{dp}{dt}\right)_v$ [1]):

$$\lambda = \int_{v_1}^{v_2} \left(\frac{a - Ta'}{v^2} + \frac{RT^2\, b'}{(v-b)^2} \right) dv = \frac{a - Ta'}{v_1} + \frac{RT^2\, b'}{v_1 - b} - {\scriptstyle \text{corr. } v_2},$$

when we may consider b and b' as independent of v in Helium, at least on the liquid branch. When we again subsitute $a^+/_v : RT$ for $v : (v-b)$ (see above), we get (substituting v for v_1):

$$\lambda\, v = (a - Ta') + \frac{a^+}{v}\, Tb' - {\scriptstyle \text{corr. } v_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

The value of λ in this equation can be calculated from the experimental values of p, v_1 and v_2. (Cf the Second Part of this paper).

In this equation $b' = -(\beta - 2\,\delta T)$ can be eliminated at 2°,3 by means of (1). We then obtain:

$$\lambda\, v = (a_0 + \gamma T^2) - \frac{a_0 + \gamma T^2 + {\scriptstyle pv^2}}{a^+/_v}\, RT - {\scriptstyle \text{corr. } v_2},$$

i. e.

$$\underline{\lambda\, v \left(1 + \frac{v_1}{v_2} \right) = (a_0 + \gamma T^2) \left(1 - \frac{RT}{a^+/_v} \right) - {\scriptstyle pv^2}\, \frac{RT}{a^+/_v} \quad (2^\circ{,}3),} \quad . \quad (3)$$

---

[1]) For ordinary substances, where the terms with a' and b' about cancel each other, this expression becomes simply $\lambda = \frac{a}{v_1} - \frac{a}{v_2}$, which relation was first derived by BAKKER in his Thesis for the Doctorate (1885).

in which with regard to the very slight correction for v_2 it has been taken into account, that both in (α) and in (3) the principal term is $(a_0 + \gamma T^2)$, so that in approximation λ will be $= (a_0 + \gamma T^2) : v_1 -$ ibid $: v_2$, which leads to $\lambda v_1 = (a_0 + \gamma T^2)\left(1 - \frac{v_1}{v_2}\right)$ or $\lambda v_1 \left(1 + \frac{v_1}{v_2}\right) = a_0 + \gamma T^2$, i. e. — with the addition of the other terms — to (3).

A *fourth* relation follows from (α), when $T = 0$ is put. Then follows

$$\underline{\lambda_0 v_0 = a_0}\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which λ_0 and v_0 are known from experimental data. For we have from the vapour-pressure equation $log^{10} p = -{}^{A}/_{T}$ + etc., in which $2.3026\,A = 3{,}8308 \times 2.3026 = {}^{\lambda_0}/_{R}$ (see § 1 of the Second Part), with $R = 1 : 273{,}09 = 0{,}0036618$:

$$\lambda_0 = 3{,}8308 \times 0{,}0036618 \times 2{,}3026 = \underline{0{,}03230} \text{ (in norm. units).}$$

To reduce this to gr. cal. 15°, it must be multiplied by $273{,}09 \times 1{,}9866 = 542{,}63$, R being $= 1 : 273{,}09$ in normal units, and $= 1{,}9866$ in gr. cal. Then $\lambda_0 = L_0 = \underline{17{,}53}$ gr. cal. is obtained, and not $4 \times 3{,}5 = 14$ gr. cal., as VERSCHAFFELT calculated on the ground of in my opinion unfounded suppositions.

Now from $\underline{D_0 = 0{,}1458^6}$ (this value will be found in § 3) follows in normal units:

$$v_0 = \frac{4}{22416\,D_0} = \frac{0{,}000178444}{D_0},$$

so that $10^6 v_0$ becomes $\underline{= 1223{,}4}$, and further according to (4):

$$a_0 = 0{,}03230 \times 1223{,}4 . 10^{-6} = \underline{39{,}515 . 10^{-6}},$$

against $a_k = \underline{67{,}42 . 10^{-6}}$; in consequence of which $a_0 : a_k$ becomes $= 0{,}5861 = 0{,}6$. For ordinary substances this relation is about 1,6.

With this value of a_0 we can now determine α and γ from (2) and (3). According to table IX in the Second Part λ is at 2°,3 $= 0{,}03060$, $v_1 = 1215 . 10^{-6}$, hence $\lambda v_1 = 37{,}18 . 10^{-6}$. And $v_1 : v_2$ being $= 1 : 93$ at 2°,3, $\lambda v_1 (1 + {}^{v_1}/_{v_2})$ becomes $= 37{,}58 . 10^{-6}$.

At 2°,3 the correction term $p v_1{}^2 (RT : {}^{a+}/_{v_1})$ is $= 0{,}06959\, (1215)^2 . 10^{-12} \times (0{,}008422 \times 1215 . 10^{-6} : 59{,}41 . 10^{-6})$, in which p is expressed in atm. (Table V), while for a at 2°,3 presently $59{,}31 . 10^{-6}$ will be found, to which then $0{,}10 . 10^{-6}$ is added as correction on a, viz. (see before (1)) $p v_1{}^2 = 0{,}06959 \times (1215)^2 . 10^{-12} = 0{,}06959 \times 1{,}476 . 10^{-6} = 0{,}1027 . 10^{-6}$.

We then find for the correction term in question:

$$0{,}103 . 10^{-6} \times (10{,}233 . 10^{-6} : 59{,}41 . 10^{-6}) = 0{,}103 . 10^{-6} \times 0{,}172 = 0{,}0177 . 10^{-6} = 0{,}02 . 10^{-6}.$$

Hence (3) becomes:

$$37{,}58\,.\,10^{-6}+0{,}02\,.\,10^{-6}=$$
$$=\left(39{,}515\,.\,10^{-6}+5{,}29\,\gamma\right)\left(1-\frac{0{,}008422\times 1215\,.\,10^{-6}}{(39{,}515\,.\,10^{-6}+2{,}3\,\alpha-5{,}29\,\gamma)^{+}}\right).$$

Now according to (2) $5{,}19\,.\,10^6\alpha-26{,}94\,.\,10^6\gamma=67{,}42-39{,}515=27{,}905$, hence $10^6\alpha-5{,}19\,.\,10^6\gamma=5{,}3767$, and therefore $2{,}3\,.\,10^6\,\alpha=12{,}366+$ $+11{,}94\,.\,10^6\gamma$. Substituting this in the above equation, the result is

$$37{,}60=(39{,}515+5{,}29\,.\,10^6\gamma)\left(1-\frac{10{,}233}{(51{,}881+6{,}65\,.\,10^6\gamma)^{+}}\right),$$

in which the correction factor at a^{+} amounts to $=0{,}103:59{,}31=$ $=0{,}00173=1:600$ of the value, according to the above.

In consequence of this we get:

$$39{,}515+5{,}29\,.\,10^6\gamma=\frac{37{,}60}{1-\dfrac{10{,}233}{51{,}971+6{,}661\,.\,10^6\gamma}},$$

i.e.

$$(39{,}515+5{,}29\,.\,10^6\gamma)\,(41{,}738+6{,}661\,.\,10^6\gamma)=37{,}60\,(51{,}971+6{,}661\,.\,10^6\gamma),$$

leading to

$$35{,}237\,(10^6\gamma)^2+233{,}54\,.\,10^6\gamma-304{,}8=0,$$

or $(10^6\,\gamma)^2+6{,}622\,.\,10^6\,\gamma-8{,}650=0$, yielding $10^6\,\gamma=1{,}1177$; and further (see above) $10^6\,\alpha=5{,}3767+5{,}19\times 1{,}1177=11{,}178$. We then finally find for a:

$$\underline{10^6\,a=39{,}515+11{,}178\,T-1{,}1177\,T^2}\ \text{(valid to a little further than } T_k\text{)},\quad (5)$$

in which accidentally the coefficient of T^2 is exactly $=0{,}1$ of that of T. Hence for a the formula gives a maximum at exactly 5°, i. e. $=67{,}46\,.\,10^{-6}$. After this a will decrease, approaching a limiting value at $T=\infty$ (see Fig. 3), which is, of course, not rendered by (5). Now the following values for a are calculated from (5).

$T=$	0°	0°,5	1°,4	2°,3	5°,0	5°,2 abs.
$10^6\,a=$	39,515	$44{,}82\overline{5}$	52,973	59,311	67,46	67,42

The value 59,31 at 2°.3 has already been used above for the calculation of the small correction term.

From (1) the value of $-b'=\beta-2\,\delta T$ at 2°,3 can now be calculated. We find:

$$-b'=\frac{(a_0+\gamma T^2+pv^2)\,R}{(a^{+}/v)^2}=\frac{(39{,}515+5{,}913+0{,}103)\,10^{-6}\times 0{,}0036618}{(59{,}414:1215)^2}.$$

For at 2°,3 $10^6\,a$ is $=59{,}311$, which becomes $=59{,}414$ with the correction 0,103 (see above). Hence we get:

$$-10^6\,b'=0{,}16673\times(20{,}450)^2=\text{ibid.}\times 418{,}20=\underline{69.73}\ (2°{,}3).$$

Thus from the fact of the maximum density at 2°,3, and making use of the values of λ_0 and $\lambda_{2.3}$ to be calculated from the experimental material, we have determined the whole course of a, and have succeeded at the same time in finding out something about the quantity b, viz. $-b' = \beta - 2\delta T$.

Assuming again $10^6 v_0 = 1223{,}4$, the coefficients β and δ in $b = b_0 - \beta T + \delta T^2$ can easily be determined, now that a is known, from two observations of the liquid density, e.g. at 1°,4 and at 2°,3. Of course we might also have determined $b_0 = v_0$, β and δ from three such observations, but — now that the value of v_0 has once been established (see § 3) — we prefer the method of calculation indicated, the more so because we then also possess a means to *test* the value of $-10^6 b'$ at 2°,3 found just now, i. e. about 70.

From the equation of state follows:

$$\left.\begin{array}{l|l} T = 1^\circ{,}4 & 0{,}003822 + \dfrac{52{,}973 \,.\, 10^{-6}}{(1222{,}5)^2 \,.\, 10^{-12}} (1222{,}5 - 10^6 b_{1.4})\, 10^{-6} = 0{,}005127 \\ T = 2^\circ{,}3 & 0{,}06959 + \dfrac{59{,}311 \,.\, 10^{-6}}{(1215)^2 \,.\, 10^{-12}} (1215 - 10^6 b_{2.3})\, 10^{-6} = 0{,}008422 \end{array}\right\} ,$$

in which the values of a were determined just now, those of p and v (calculated from D) having been experimentally given (Table V and VII). This yields therefore:

$$\left.\begin{array}{l} (0{,}004 + 35{,}445)\ (1222{,}5 - 10^6 b_{1.4}) = 5127 \\ (0{,}070 + 40{,}178)\ (1215 \quad - 10^6 b_{2.3}) = 8422 \end{array}\right\} ,$$

from which $1222{,}5 - 10^6 b_{1.4} = 144{,}63$, $1215 - 10^6 b_{2.3} = 209{,}25$, hence

$$10^6 b_{1.4} = 1077{,}87 \quad ; \quad 10^6 b_{2.3} = 1005{,}7\overline{5}.$$

From this, and with $10^6 b_0 = 1223{,}4$, follows immediately:

$$\underline{10^6 b = 1223{,}4 - 118{,}4\overline{5}\, T + 10{,}356\, T^2} \text{ (valid to } \pm 2^\circ{,}3) \quad . \quad . \quad (6)$$

From this follows, therefore, $10^6 b'_{2.3} = 118{,}4\overline{5} - 20{,}71 \times 2{,}3 = \underline{70{,}82}$, against 69,73 above, or round 71 against 70. Hence the maximum of density lies possibly not *exactly* at 2°,3; it is also possible that the slight dependence of b on the volume at 2°,3, which has been neglected in the beginning, is already perceptible ^{1}).

3. The minimum of density at 0°,52. Formula for D_1.

From the equation for $T\left(\dfrac{dp}{dt}\right)_v$ in the beginning of § 2, after substi-

---

^{1}) In this connection we remark that from the above formulae, which of course remains valid to T_k, when only the volume is kept $= v_0$, it would follow that $10^6 (b_{v_0})_k = \underline{888}$, $10^6 b_k$ being $= \underline{1051}$ (from T_k and p_k). It would then follow from this, according to a formula derived by me (Zeitschr, f. anorg. u. allg. Chem. **149**, p. 349 (1925)), that $(b_\infty)_k : b_k$ is $= \dfrac{1}{2}\left(\dfrac{1051}{888} + 1\right) = 1{,}09$, hence $10^6 (b_\infty)_k = \underline{1146}$. From this it is possible, at least at T_k, to judge to some extend about the variability of b with the volume. Between $v = v_0$ and $v = \infty$ the value of b then varies from 888 to 1146, i. e. in the ratio of 1 : 1,3.

tution of the value for $\left(\frac{v}{v-b}\right)^2$, follows:

$$T\left(\frac{dp}{dt}\right)_v v^2 = a_0 + \gamma T^2 + {\scriptstyle pv^2} - \left(\frac{a^+}{v}\right)^2 \frac{\beta - 2\,\delta T}{R}.$$

At $T=0$ this becomes:

$$a_0 - \left(\frac{a_0}{v_0}\right)^2 \frac{\beta}{R} = a_0\left(1 - \frac{a_0}{v_0{}^2}\frac{\beta}{R}\right).$$

Now

$$1 - \frac{a_0}{v_0{}^2}\frac{\beta}{R} = 1 - \frac{39{,}515 \,.\, 10^{-6}}{(1223{,}4)^2 .\, 10^{-12}} \times 118{,}4\overline{5} \,.\, 10^{-6} \times 273{,}09,$$

i.e. with $(1{,}2234)^2 = 1{,}4967$:

$$1 - 26{,}401 \times 118{,}4\overline{5} \,.\, 10^{-6} \times 273{,}09 = 1 - 0{,}854 = 0{,}15.$$

And $\left(\frac{dv}{dt}\right)_v$ always having the same sign as $\left(\frac{dp}{dt}\right)_v$ (see § 2), hence also as $T\left(\frac{dp}{dt}\right)_v . v^2$, with Helium $\left(\frac{dv}{dt}\right)_p$ will be **positive** at the absolute zero. And since there is a minimum at 2°.3, there will *necessarily* be also a maximum volume at lower temperature, i.e. a **minimum density** See Fig. 1), and this in the neighbourhood of 0°,52, as we shall presently see.

In general it follows from the above relation, that $\left(\frac{dv}{dt}\right)_p$ will be *positive* at $T=0$, when

$$\frac{\beta}{b_0} < \frac{R}{{}^{a_0}/_{b_0}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This is fulfilled in Helium, owing to the small value of a (low critical temperature). But how is this with ordinary substances with comparatively high critical temperature? For such substances $a_0 \sim 1{,}6\, a_k$, $b_0 \sim 0{,}5\, b_k$, hence $a_0 : b_0 = 3{,}2\,(a_k : b_k)$. With $\lambda = {}^{27}/_{28}$ it follows from $RT_k = {}^{8}/_{27}\, \lambda\, {}^{a_k}/_{b_k}$, that $a_k : b_k$ is $= {}^{7}/_{2}\, RT_k$, so that for ordinary substances $a_0 : b_0$ will be about $= 11\, RT_k$. For a positive initial course $\beta : b_0$ must, therefore, be $< 1 : 11\, T_k$, which would yield $\beta : b_0 < 1 : 6000$ with e.g. $T_k = 550°$ abs.

Now it is, of course, *possible* that β is so small, and then v will immediately increase, without maximum or minimum, however. For if this were the case, it would follow that $(a_0 + \gamma T^2)$ — etc. could become $=0$, which with such small values of β is evidently impossible.

But generally β will, no doubt, be greater. And then v begins with a *decrease*, because then $\left(\frac{dv}{dt}\right)_p$ is negative. But because v must of course, increase later on, there must neccessarily be a minimum volume (maximum density) in this (most frequently occurring) case. Accordingly, the phenomenon of a maximum density would not remain restricted to Helium, but would have to be found for any substance (provided β be not *too* small) at low temperature — without the minimum, however, at still lower temperature. But unfortunately an "ordinary" substance becomes solid long before the temperature, at which this phenomenon could appear, is reached. And above the melting-point, *a* just as *b* decreases with the temperature, so that then the phenomenon cannot possibly be realized (see below).

The possibility of a maximum and a minimum in Helium can very simply be represented in a diagram in the following way. If the terms γT^2 and pv^2, whose values are small compared with the other terms, are disregarded, the sign of $\left(\frac{dv}{dt}\right)_v$ is chiefly determined by that of $a_0 - q \times r$, in which for Helium $q = ({}^a/_v)^2$ is an *increasing* quantity owing to $a = a_0 + \alpha T \ldots$ (v varies then exceedingly little), and $r = (\beta - 2\,\delta T) : R$ is a *decreasing* quantity. This may e. g. give rise to what follows (the figures are entirely arbitrary).

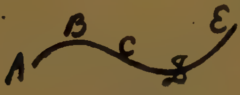

Fig. 4

$$\begin{array}{lllll}
4000 - 37.5 \times 105 = 4000 - 3937.5 & = + & 62.5 & (A \text{ in Fig. 4}) \\
4000 - 40 \times 100 = 4000 - 4000 & = & 0 & (B \text{ ,, ,, ,,}) \\
4000 - 45 \times 90 = 4000 - 4050 & = - & 50 & (C \text{ ,, ,, ,,}) \\
4000 - 50 \times 80 = 4000 - 4000 & = & 0 & (D \text{ ,, ,, ,,}) \\
4000 - 55 \times 70 = 4000 - 3850 & = + & 150 & (E \text{ ,, ,, ,,}) \\
\end{array}$$

etc.

Here the quantity *b* itself must, of course, also decrease (β positive). For else we should get (see above) $a_0 + q \times r$ (instead of $a_0 - q \times r$), which of course, could never become $= 0$. Nor can the phenomenon, of course, be found with *a* diminishing at the same time with *b* (e. g. for ordinary substances above the melting-point, (see above), since $\left(\frac{dv}{dt}\right)_p$ being once positive, becomes then greater and greater positive (*q* and *r* *both* decrease).

Let us now examine *where* the minimum of density in Helium lies. For this purpose T must be solved from

$$(a_0 + \gamma T^2) - \left(\frac{a}{v}\right)^2 \frac{\beta - 2\,\delta T}{R},$$

where *a* is $a = a_0 + \alpha T - \gamma T^2$, the correction term pv^2 being certainly negligible at $0^\circ{,}5$ ($p = 0{,}0_73$ atm. !). After some trials the following value is soon found:

$$\underline{T_{\text{min.}} = 0^\circ{,}521.}$$

For then the above expression becomes:

$$(39{,}515 + 0{,}304)\, 10^{-6} - \left(\frac{45{,}039 \,.\, 10^{-6}}{1223{,}9 \,.\, 10^{-6}}\right)^2 (118{,}4\overline{5} - 10{,}79) \,.\, 10^{-6} \times 273{,}09,$$

or after division by 10^{-6}:

$$39,819 - (36,801)^2 \times 107,66 \,.\, 10^{-6} \times 273,09 = 39,819 - 1354,3 \times \text{etc.},$$

hence

$$39,819 - 39,820, \text{ i.e. } 39,82 - 39,82 = 0.$$

If, now, at low temperatures the liquid density is represented by the quadratic formula $D = D_0 - \varepsilon T + \varphi T^2$, already $\varepsilon : 2\varphi$ is $= 0,521$ on account of the minimum at $0^\circ,521$. If, further, we assume the experimental values $D_{1^\circ,2} = 0,1459$ and $D_{1^\circ,9} = 0,1462$, we find easily from

$$D = D_0 - 1,042\,\varphi T + \varphi T^2:$$

$$10^4\,\varphi = 2,082\bar{5}, \quad 10^4\,D_0 = 1458,605, \text{ and further } 10^4\,\varepsilon = 2,1700,$$

so that at low temperatures the liquid densities may be represented by

$$\underline{10^4\,D_1 = 1458,6 - 2,170\,T + 2,082\,T^2} \text{ (valid up to } \pm 2^\circ). \quad . \quad (8)$$

It is the above value of D_0, that we have assumed in our calculations in § 2. If we had assumed a slightly different value, the value found now would *not* have been in perfect harmony with it. Through some repeated new calculations the right value, which leads to a value in (8) identical with it, is finally found. This formula gives the following values of D_1 and $v_1 = 178,444 \,.\, 10^{-6} : D_1$ (see § 2).

TABLE A.

T	$10^4\,D_1$	$10^6\,v_1$	T	$10^4\,D_1$	$10^6\,v_1$
0	1458.61	1223.39	1.2	1459.00	1223.1
0.5	**1458.04**	**1223.86**	1.3	1459.30	1222.8
0.6	1458.05	1223.85	1.4	1459.6$\bar{5}$	1222.5
0.7	1458.11	1223.80	1.5	1460.04	1222.2
0.8	1458.20	1223.7	1.6	1460.46	1221.8
0.9	1458.34	1223.6	1.7	1460.93	1221.4
1.0	1458.52	1223.$\bar{5}$	1.8	1461.4$\bar{5}$	1221.0
1.1	1458.74	1223.3	1.9	1462.00	1220.5

At 2° the formula gives 1462,6; experimentally round 1463 has been found. (At $1^\circ,6$ the value according to the formula is $1460,\bar{5}$, round 1460 having been found experimentally). Hence the minimum of density at $0^\circ,52$ is $= 0,1458$; we know that D_1 at $2^\circ,3$ reaches the maximum 0,1469. The values of D_1 between 0° and 1°, therefore, do not differ much, they are always in the neighbourhood of 0,1458; only after this they begin to rise somewhat. The course is then *quite conformable* to the graphical representation given in Comm. 170^b.

4. The minimum of λ at 1°,5.

Also the molecular internal latent heat λ, which passes through a maximum at 3°,4, will again pass through a *minimum* at about 1°,5, as does not only follow from the values of λ calculated from $\frac{dp}{dt}$ and $v_2 - v_1$ (see Table IX), but can also be demonstrated theoretically.

We saw above in § 2, that

$$\lambda = \frac{a_0 + \gamma T^2}{v} - \frac{a}{v^2}\, T\,(\beta - 2\,\delta T),$$

when the corrections are omitted, which disappear at very low temperatures, and of course at $T = 0$. Then it follows from this, when we suppose v along the saturation line to be constant, which is about fulfilled in the neighbourhood of $T = 0$, that

$$\frac{d\lambda}{dT} = \frac{2\gamma T}{v} - \frac{a + Ta'}{v^2}\,(\beta - 2\,\delta T) + \frac{aT}{v^2}\,2\,\delta.$$

Hence at $T = 0$, $a + Ta' = a_0 + 2\,\alpha T - 3\,\gamma T^2$ then being $= a_0$, we have:

$$\underline{\left(\frac{d\lambda}{dT}\right)_0 = -\frac{\beta a_0}{{v_0}^2}}, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

which is, accordingly, **always negative.** (See Fig. 2).

For *ordinary* substances, where the variability of v cannot be neglected, there is, besides, still a term $-\frac{a_0}{{v_0}^2}\left(\frac{dv}{dt}\right)_0$. This is then even the principal term, as β is then small in comparison with $\left(\frac{dv}{dt}\right)_0$. It now follows from the equation of state, that when a and b are constant (ideal substances), this term is $= -R$, and *greater negative*, when the substances are not ideal. λ, therefore, decreases continually, from $T = 0$ to T_k, without minimum or maximum, as in Helium (see further).

As regards $L = \lambda + RT$ (at low temperatures $p\,(v_2 - v_1) = RT$), this will be $\left(\frac{dL}{dt}\right)_0 = -R + R = 0$ for ordinary substances, when they are ideal substances, and *negative* when they are not ideal substances.

Now from (9) follows for *Helium*:

$$\left(\frac{d\lambda}{dT}\right)_0 = -\frac{118{,}4\bar{5}\,.\,10^{-6} \times 39{,}515\,.\,10^{-6}}{(1223{,}4)^2 .\ 10^{-12}} = \underline{-0{,}003127},$$

theoretically. Experimentally the following value is found (see Table IX) between 0° and 0°,5:

$$(0{,}03091 - 0{,}03230) : 0{,}5 = -0{,}0028.$$

This is the chord between the said temperatures. Hence for the tangent a somewhat greater (negative) value must be found (see Fig. 2), so that

$-0{,}0031$ may be right. If to this $R=0{,}0036618$ is added, then the following value holds for Helium:

$$\left(\frac{dL}{dT}\right)_0 = +\,0{,}000535,$$

i.e. **positive**. Also this value proves to be in good agreement. For according to Table IX $(0{,}03274-0{,}03230):0{,}5=0{,}00088$ is found for it between 0° and 0°,5, and $(0{,}03399-0{,}03274):0{,}5=0{,}00250$ between 0°,5 and 1° (which points to a *point of inflection* between $T=0$ and the maximum at 3°,5; see Fig. 2). The value of $10^5\left(\frac{dL}{dt}\right)_0$ will, therefore, be pretty considerable smaller than 88, so that again 53,5 may be correct.

L increases, therefore, at first, and as this quantity will necessarily rapidly approach to 0 in the neighbourhood of T_k, in consequence of the factor $\frac{1}{v_1}-\frac{1}{v_2}$, there must also necessarily be a **maximum** at L, which is, indeed, found at 3°,5 (cf. Table IX).

Now it follows from the experimental data, that not only L presents a *maximum*, but also λ, and this at 3°,4 (Table IX). And because λ at first *decreases*, there must *necessarily*, besides this maximum, be also present a **minimum** for λ at low temperature. This, too, is confirmed experimentelly. According to Table IX this minimum lies between 1°,4 and 1°,5, but nearer to 1°,5. *Theoretically* 1°,47 is found for it, as appears from what follows.

At this temperature

$$(2{,}2354\,.\,10^{-6}\times 1{,}47\times 1222{,}3\,.\,10^{-6})-(a_0+2\alpha T-3\gamma T^2)\times$$
$$\times\,(118{,}45-20{,}71\times 1{,}47)10^{-6}+(a_0+\alpha T-\gamma T^2)\times 1{,}47\times 20{,}71\,.\,10^{-6}$$

is found for

$$v^2\frac{d\lambda}{dT}=2\gamma Tv-(a_0+2\alpha T-3\gamma T^2)(\beta-2\delta T)+(a_0+\alpha T-\gamma T^2)\,T\,.\,2\delta.$$

Now $10^6\,(a_0+\alpha T-\gamma T^2)=39{,}515+11{,}178\times 1{,}47-1{,}1177\times\times(1{,}47)^2=39{,}515+16{,}432-2{,}415=53{,}532$. And $10^6(a_0+2\alpha T-3\gamma T^2)==39{,}515+32{,}864-7{,}245=65{,}134$. Hence, multiplying by 10^{12}, the above becomes, with $118{,}45-30{,}444=88{,}006$:

$$10^{12}\,v^2\frac{d\lambda}{dT}=4016{,}5-5732{,}2+1629{,}9=-\,85{,}8.$$

To this should be added 101,2 of a correction term with $\frac{dv}{dt}$, viz.

$$\left[-\frac{a_0+\gamma T^2}{v^2}+\frac{2\alpha T(\beta-2\delta T)}{v^3}\right]\frac{dv}{dT}\times 10^{12}\,v^2,$$

i.e.

$$\left[(a_0+\gamma T^2)-\frac{2\alpha T(\beta-2\delta T)}{v}\right]\times\left(-\frac{dv}{dT}\right)\times 10^{12}.$$

Now $-\dfrac{dv}{dt}$ is at 1°,47 (see Table A in § 3, or formula (8) for D_1) $= 3{,}307 \, . \, 10^{-6}$. With $10^6 (a_0 + \gamma T^2) = 39{,}515 + 2{,}415 = 41{,}93$ this correction term, therefore, becomes:

$$\left[41{,}93 - \frac{2 \times 53{,}532 \times 1{,}47 \times 88{,}006}{1222{,}3}\right] \times 3{,}307,$$

or

$$(41{,}93 - 11{,}33) \times 3{,}307 = 30{,}60 \times 3{,}307 = 101{,}2.$$

Hence we get at 1°,47:

$$10^{12} \, v^2 \frac{d\lambda}{dT} = -85{,}8 + 101{,}2 = +14{,}4.$$

At 1°,48 we would have found in the same way:

$$(4043{,}7 - 5729{,}5 + 1643{,}2) + (-100) = +57.$$

And at 1°,4 we get $(3826 - 5747 + 1536) + (-90) = -295$, from which it is therefore seen, that at slightly below 1°,47 $\dfrac{d\lambda}{dT}$ passes through 0. At 1°,46 this quantity is already about —30; all this in perfect harmony with Fig. 2 in connection with the values of λ, calculated from the experimental data (Table IX).

We once more point out how accurate the results are (also quantitatively) to which the formulae for a and b, determined from observations at 2°,3, lead; also in the neighbourhood of $T = 0$ and at very low temperatures (minimum D_1 and λ resp. at 0°,5 and 1°,5). We may, therefore, safely put aside the value $L_0 = \lambda_0 = 14$ gr. cal. of VERSCHAFFELT (based on NERNST's quite erroneous theory), and accept the value 17,5, following necessarily from the different data; which value, indeed, is in much better harmony with the observations of DANA and KAMERLINGH ONNES, whereas the value 14 would be in conflict with them. (See § 4 of the Second Part).

Physics. — „*On the Maximum and Minimum Density and the Heat of Evaporation of Helium.*" (Second Part). By Dr. J. J. van Laar. (Communicated by Prof. H. A. Lorentz).

(Communicated at the meeting of October 30, 1926).

B. Experimental Part.

1. The equation of the vapour pressure.

The experimental material is here, indeed, not very large, but still sufficient to derive a fairly reliable vapour pressure equation from it. In the following table the vapour pressures measured are given, and by the side of them the values of p calculated from the two formulae:

$$\left.\begin{aligned} log^{10}\, p^{mm} &= -\frac{3,8308}{T} + 2,9044 + 0,2107\, T \quad (0^\circ \text{ to } 4^\circ,2) \\ log^{10}\, p^{mm} &= -\frac{4,9874}{T} + 3,5083 + 0,1325\, T \quad (3^\circ,5\text{—}5^\circ,2) \end{aligned}\right\} \quad \ldots \quad (10)$$

The observations marked with an asterisk (bold type) are considered as the most accurate by the authors [1]). For this reason they have been used for the calculation of the constants in both formulae. When the

TABLE I.

T	$p^{mm}_{exp.}$	$p_{form.}$	T	$p^{mm}_{exp.}$	$p_{form.}$
1.35	(3)	2.25	***3.516**	**359.5**	359.5
***1.475**	**4.15**	4.15	3.89	565	552
2.24	51	46.4	***4.205**	**757.5**	757.5
3.17	(197)	231	4.21	760 767	761
***3.516**	**359.5**	359.5	4.90	(1329)	1380
3.89	565	549	5.04	1520	1536
***4.205**	**757.5**	757.5	5.09	1569	1596
4.21	760 767	761	5.16	1668	1681
			***5.19**	**1718**	1718

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[1]) K. Onnes, Comm. **119**^{a} (1911) and **124**^{b} (1911); K. Onnes and S. Weber, Comm. **147**^{b} (1915).

experimental values are represented grafically ($T \log p$ against T), it is at once perceived that the pressures at 1°,35, 3°,17 and 4°,90 (placed between brackets by us) are *not* in conformity with the others (one too high, the two others too low), and can, therefore, be left out of consideration in the calculation of the formulae. If this is overlooked, it leads of course to great disappointment, and the method of least squares will be of no use; which method is mathematical nonsense with a comparatively small number of observations. In contrast with the said values, those at 2°,24, 3°,89, 5°,04 and 5°,16 are in pretty good harmony with the others.

The coefficient 4,9874 in our second formula, of course, lacks the physical meaning of the corresponding coefficient 3,8303 in the first formula, viz. $= \lambda_0 : R$, because the second formula is only valid to 3°,5 downwards.

The onlogically built formula of Comm. 147*b*, where the constant 7,98 instead of 3,83 is much too high, suffers from the same evil. Terms wish $^1/_{T^2}$ and $^1/_{T^3}$ may occur neither in a theoretical, nor in an empirical formula. At low temperatures $\log p$ must approach to $-{}^A/_T$, whereas according to the formula mentioned $\log p$ would approach to $-{}^{A'}/_{T^3}$, which is an absurdity. Already in the neighbourhood of 2°,4 it gives much too low values for p 1).

If we wish to construct a theoretical formula, which is valid throughout the *whole* region, the variability of a with T, of b with T and v, and of v_1 with T must be taken into account over a great range; in any case an equation arises of the form $\log p = -\frac{A}{T} + B \log T + C + DT + ET^2 \ldots$ But this problem is particularly difficult for Helium with its deviating behaviour at lower temperatures.

In the following table the values of p have been calculated according to both formulae from 0,1 to 0,1 degree. At the same times the values of $F = \frac{T}{p}\frac{dp}{dt} = T\frac{d \log p}{dt}$ are then obtained. For from our equation $\log^{10} p = -\frac{A}{T} + C + DT$ follows immediately $F = \left(\frac{A}{T} + DT\right) \times 2{,}3026$, of which the terms $\frac{A}{T}$ and DT are, therefore, already known from the calculation of $\log^{10} p$. The accurate knowledge of F is necessary for the calculation of

$$\left.\begin{aligned} L = T\frac{dp}{dt}(v_2 - v_1) = F \times p\,(v_2 - v_1) = F \times W \\ \text{and} \qquad \lambda = L - p\,(v_2 - v_1) = L - W = (F-1)\,W \end{aligned}\right\} \quad . \; . \quad (11)$$

which quantities we shall calculate in § 4.

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1) Cf. also Note 2) added to Table IV.

TABLE II.

a. Values of p and F between 0° and 4°.2.

T	$\frac{3.8308}{T}$	$0.2107\,T$	$\log^{10} p^{mm}$	p^{mm}	$F:2.3026$	F
0	∞	0	$-\infty$	0	∞	∞
0.5	7.6616	0.1054	$-$ 4.6518	0.0_4223	7.7670	17.88
0.6	6.3847	0.1264	$-$ 3.3539	0.0_3443	6.5111	14.99
0.7	5.4726	0.1475	$-$ 2.4207	0.0_2380	5.6201	12.94
0.8	4.7885	0.1686	$-$ 1.7155	0.0193	4.9571	11.41
0.9	4.2564	0.1896	$-$ 1.1624	0.0688	4.4460	10.24
1.0	3.8308	0.2107	$-$ 0.7157	0.1924	4.0415	9.306
1.1	3.4825	0.2318	$-$ 0.3463	0.4505	3.7143	8.553
1.2	3.1923	0.2528	$-$ 0.0351	0.9224	3.4451	7.933
1.3	2.9468	0.2739	$+$ 0.2315	1.704	3.2207	7.416
1.4	2.7363	0.2950	0.4631	$2.90\overline{5}$	3.0313	6.980
1.5	2.5539	0.3161	0.6666	4.641	2.8700	6.608
1.6	2.3943	0.3371	0.8472	7.034	2.7314	6.289
1.7	2.2534	0.3582	1.0092	10.21	2.6116	6.013
1.8	2.1282	0.3793	1.1555	14.31	2.5075	5.774
1.9	2.0162	0.4003	1.2885	19.43	2.4165	5.564
2.0	1.9154	0.4214	1.4104	25.73	2.3368	5.381
2.1	1.8242	0.4425	1.5227	33.32	2.2667	5.219
2.2	1.7413	0.4635	1.6266	42.33	2.2048	5.077
2.3	1.6656	0.4846	1.7234	52.89	2.1502	4.951
2.4	1.5962	0.5057	1.8139	$65.1\overline{5}$	2.1019	4.840
2.5	1.5323	0.5268	1.8989	79.23	2.0591	4.741
2.6	1.4734	0.5478	1.9788	95.24	2.0212	4.654
2.7	1.4188	0.5689	2.0545	113.4	1.9877	4.577
2.8	1.3681	0.5900	2.1263	133.8	1.9581	4.509
2.9	1.3210	0.6110	2.1944	$156.\overline{5}$	1.9320	4.449
3.0	1.2769	0.6321	2.2596	181.8	1.9090	4.396
3.1	1.2357	0.6532	2.3219	209.8	1.8889	4.349
3.2	1.1971	0.6742	2.3815	240.7	1.8713	4.309
3.3	1.1608	0.6953	2.4389	274.7	1.8561	4.274
3.4	1.1267	0.7164	2.4941	312.0	1.8431	4.244
3.5	1.0945	0.7375	2.5474	352.7	1.8320	4.218
3.6	1.0641	0.7585	2.5988	397.0	1.8226	4.197
3.7	1.0354	0.7796	2.6486	445.2	1.8150	4.179
3.8	1.0081	0.8007	2.6970	497.7	1.8088	$4.16\overline{5}$
3.9	0.9823	0.8217	2.7438	554.4	1.8040	4.154
4.0	0.9577	0.8428	2.7895	615.9	1.8005	4.146
4.1	0.9343	0.8639	2.8340	682.3	1.7982	4.141
4.2	0.9121	0.8849	2.8772	753.7	1.7970	4.138

b. **Values of p and F between 3°.5 and 5°.2.**

T	$\frac{4.9874}{T}$	$0.1325\ T$	$\log^{10} p^{mm}$	p^{mm}	$F:2.3026$	F
3.5	1.4250	0.4638	2.5471	$352.\bar{5}$	1.8888	4.349
3.6	1.3854	0.4770	2.5999	398.0	1.8624	4.288
3.7	1.3479	0.4903	2.6507	447.4	1.8382	4.233
3.8	1.3125	0.5035	2.6993	500.4	1.8160	4.182
3.9	1.2788	0.5168	2.7463	557.6	1.7956	$4.13\bar{5}$
4.0	1.2469	0.5300	2.7914	618.6	1.7769	4.091
4.1	1.2164	0.5433	2.8352	684.2	1.7597	4.052
4.2	1.1875	0.5565	2.8773	753.9	1.7440	4.016
4.3	1.1599	0.5698	2.9182	828.3	1.7297	3.983
4.4	1.1335	0.5830	2.9578	907.4	1.7165	3.952
4.5	1.1083	0.5963	2.9963	991.5	1.7046	3.925
4.6	1.0824	0.6095	3.0336	1080	1.6937	3.900
4.7	1.0611	0.6228	3.0700	1175	1.6839	3.877
4.8	1.0390	0.6360	3.1053	1274	1.6750	3.857
4.9	1.0178	0.6493	3.1398	1380	1.6671	3.839
5.0	0.9975	0.6625	3.1733	1490	1.6600	3.822
5.1	0.9779	0.6758	3.2062	1608	1.6537	3.808
5.2	0.9591	0.6890	2.2382	1731	1.6481	$3.79\bar{5}$

Hence we find for the value of F at the critical temperature 5°,19:

$$F_k \doteq 1{,}6487 \times 2{,}3026 = 3{,}7963 = \underline{3{,}80}.$$

The almost identical values of p between 3°,5 and 4°,2, obtained with the two formulae, may now simply be averaged. The values of F should be treated in another way. Care should be taken, that the two parts F_1 and F_2 in the added graphical representation (see Fig. 5) pass continuously into each other (denoted by the line ×××××). For this purpose the differences $\triangle$ should only be gradually decreased from 35 (between 3°.2 and 3°.3) to 27 (between 4°.4 and 4°.5). Cf. Table c.

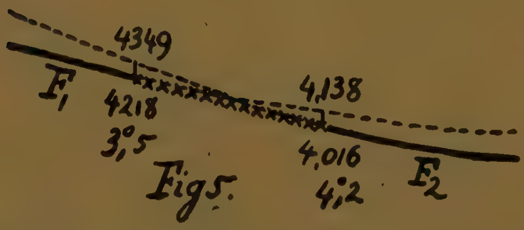

Fig 5.

c. Adjusted values between 3°.5 and 4°.2.

T	p_1	p_2	p	F_1	Δ	F_2	Δ	F	Δ
3.2	240.7	—	240.7	4.309		—		4.309	
3.3	274.7	—	242.7	4.274	35	—		4.274	35
3.4	312.0	—	312.0	4.244	30	—		4.242	32
3.5	352.7	352.5	352.6	4.218	26	4.349		4.212	30
3.6	397.0	398.0	397.5	4.197	21	4.288	61	4.183	29
3.7	445.2	447.4	446.3	4.179	18	4.233	55	4.154	29
3.8	497.7	500.4	499.1	4.165	14	4.182	51	4.125	29
3.9	554.4	557.6	556.0	4.154	11	4.135	47	4.096	29
4.0	615.9	618.6	617.2	4.146	8	4.091	44	4.067	29
4.1	682.3	684.2	683.3	4.141	5	4.052	39	4.038	29
4.2	753.7	753.9	753.8	4.138	3	4.016	36	4.009	29
4.3	—	828.3	828.3	—		3.983	33	3.980	29
4.4	—	907.4	907.4	—		3.952	31	3.952	28
4.5	—	991.5	991.5	—		3.925	27	3.925	27

2. The second Virial-Coefficient B and the vapour volume v_2. For the calculation of the values of v_2 (required for $W = p\,(v_2 - v_1)$), the values of B in

$$pv_2 = RT + \frac{B}{v_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

should be rather accurately known. Only at very low temperatures (to about 0°,7) $pv_2 = RT$ may be put; the deviations soon become pretty great for Helium, much greater than for "ordinary" substances. The values of B, calculated in the following table, have been derived from the formula

$$10^6 B = (-44{,}9 + 2{,}032\,T)\,e^{\frac{1{,}155}{T}}, \quad . \; . \; . \; . \; . \; . \quad (13)$$

the coefficients of which has been calculated from the pretty certain values **512** at 0°C.; **0** at 22°,1 abs. (*Boyle point*); and **— 47,7** at 4°,23 abs.; marked in the subjoined table with an asterisk and printed in bold type. This theoretical formula was derived[1]) by me at the time in the form

$$B = (RT\varphi_1 b_k - \varphi_2 a_k)\,e^{\frac{\alpha}{T} - \frac{\alpha}{T_k}} = (-\beta_1 + \beta_2 T)\,e^{\frac{\alpha}{T}},$$

the efficiency of which has been tested by me by a number of substances

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[1]) J. de Ch. ph. 17 (1919), p. 266—324. Cf. also Zustandsgl. p. 21 et seq.

(He, H_2, Ne, Ar, O_2, N_2, CO_2, CH_3Cl). The available material of facts for *Helium* is combined in Table III.

TABLE III. [1]

T	$10^6 B_{exp.}$	$10^6 B_{formula}$
673 (400° C.)	+ 1126 (from 457 H.O.)	+ 1325
573 (300° „)	+ 986 („ 470 „)	+ 1125
473 (200° „)	+ 854 („ 493 „)	+ 919
373 (100° C.)	+ 701 (from 513 H.O.); K.O. 493 at 100°.35	+ 716*
323 (50° „)	+ 619 („ 523 „)	+ 614*
293 (20° „)	+ 534 („ 448 K.O.)	+ 553*
*273.09 (0° „)	+ 512 (K.O.; 529 H.O.)	+ 512
169.52	+ 337 (from 543 K.O.)	+ 302
90.34	+ 176 („ 532 „)	+ 141
69.86	+ 100.3 (v. A.; K.O.)	+ 98.7*
56.53	(+ 96.0) (from 464 K.O.)	+ 71.4
55.68	(+ 97.0) („ 476 P.; K.O.)	+ 69.6
*22.1 (BOYLE-p.)	0 (v. A.; K.O. grafically from †)	0
20.55	− 4.2 † (v.A.; K.O.)	− 3.4 (20°.5)*
53	− 9.0	
51	− 9.1	
48	− 7.4 (from − 99 Pal.; K.O.)	
20.37	(+ 3.0) („ + 40 K.O.*)	− 3.7
18.22	(− 24.4) † (v.A.; K.O.)	− 8.4
16.55	(− 24.5)	− 12.1
14.27	− 11.4 (from − 211 K.O.*)	− 17.3
4.71	− 45.9 (from D_2 M.; Cr.; K.O.; Sw.)	− 45.2 *
59	− 46.9	− 45.7
29	− 47.0 (from − 2990 K.O.**)	− 47.4
*4.23	− 47.7 („ D_2 M. — Sw.)	− 47.7

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[1] The addition: "from 457 H. O." means that 457 must be multiplied by $1 + 0{,}0036618\, t$. For these values refer to $pv_2 = RT\left(1 + \frac{B'}{v}\right)$, so that our $B = RTB' = (273 + t) : 273 . B' = (1 + 0{,}0036618\, t)\, B'$. ($R = 1 : 273.09$ in norm. units).

H.O. means HOLBORN en OTTO 1924; K.O. = K. ONNES, Comm. 102a; K.O.* =

In particularly good agreement are the values (marked with an asterisk) at 100°, 50° and 20° C., at 69°.9 abs., 20°,5 abs. (—4.2 against calculated — 3.4) and the three values at about 4°.5 abs. The values at 56° and at 20°,4, 18°,2 and 16°,6, placed between parentheses, on the other hand, fall outside the schema, also of a graphical representation. and may, therefore, be ignored. We may, therefore, safely use the formula (13) for the calculation of the *B*-values at some temperatures below the critical temperature, occurring in Comm. 172*b*. These values, and those below 2°,3 are necessary for the determination of D_2 for

TABLE IV.

T	$10^6 RT$	$p^{atm.}_{form.}$	$10^6 B_{form.}$	$10^6 v_{2\ calc.}$	$10^4 D_{2\ calc.}$	$10^4 D_2$ Comm. 172^b	$10^6 pv_2$ calc.	△ BOYLE in %
5.19	$1900\overline{5}$	2.2605	(—42.9) 1)	2572 3)	693.8 3)	693.0 3)	5815	69.4
4.71	17247	1.5592	—45.2	6800	262.4	269.9	1060.10	38.6
4.59	16808	1.4092	—45.7	7737	230.6	238.9 4)	1090.10	35.2
4.23	15489	1.0197	—47.7	1090.10	163.7	163.7	1111.10	28.2
4.22	15453	1.0111	—47.8	1098.10	162.5	161.8	1112.10 5)	28.0
3.90	14281	0.7316	—49.7	1499.10	119.0	117.6	1097.10	23.2
3.30	12084	0.3614	—54.2	2810.10	63.50	64.35	1016.10	16.0
2.56	9374	0.1169	—62.3	7288.10	24.48	(20.79)	8520	9.11
2.37	8678	0.08088	—65.2 2)	9916.10	17.99	(13.68) 2)	8020	7.58
2.30	8422	0.06959	—66.5	1125.10^2	15.86	(11.59)	7830	7.03
2.29	8386	0.06812	—66.7	1146.10^2	15.57	—	7804	6.94
2.21	8093	0.05699	—68.1	1330.10^2	13.42	—	7580	6.34
2.10	7690	0.04384	—70.4	1657.10^2	10.77	—	7264	5.54
1.93	7067	0.02788	—74.5	2425.10^2	7.358	—	6761	4.33
1.92	7031	0.02709	—74.8	2484.10^2	7.184	—	6729	4.30
1.59	5822	0.008897	—86.2	6392.10^2	2.792	—	5687	2.32
1.28	4687	0.001997	—104	2325.10^3	0.7675	—	4643	0.94
1.20	4394	0.001214	—111	3595.10^3	0.4964	—	4363	0.70

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ibid. Comm. 102*c*; K.O.** = ibid. Comm. 119*a*; P.; K.O. = PENNING and K.O., Comm. 165*c*; Pal.; K.O. = PALACIOS MARTINEZ and K.O., Comm. 164; v. A.; K.O. = VAN AGT and K.O., Comm. 176*b*, p. 28 (1925); M.; Cr.; K.O.; Sw. = MATHIAS, CROMMELIN, K.O. and SWALLOW, Comm. 172*b*. Compare also KEESOM and K.O., Arch. Néerl. IX, N⁰. 1 (1925).

Cf. the notes 1, 2, 3, 4 and 5 of Table IV on the following page.

the calculation of the diameter. For this reason the values of v_2, calculated from (12), resp. $D_2 = 4:22416\, v_2 = 178,444 . 10^{-6} : v_2$ (see § 2, 1st Part, after (4)), are inserted in the foregoing table by the side of those of B; and besides those of pv_2, to judge about the deviations from the law of BOYLE.

After these preliminary calculations (as said before, necessary for the calculation of the diameter, see § 3), we have again inserted all the quantities of Table IV in Table V, but now over the whole region and from 0.1 to 0,1 degree. The values of v_2 (and D_2) above 4°,7 cannot be calculated accurately by means of (12), because then the vapour volumes become too small. We have, therefore, calculated the values of D_2 (and of D_1) at these temperatures from formulae for $^1/_2(D_1+D_2)$ and $^1/_2(D_1-D_2)$ (see § 3), and then v_2 (and v_1) from D_2 (and D_1). The values of v_2 and D_2 from 4°,3 to 4°,7 (inclusive), placed between brackets, have been calculated in the same way; it is seen that they differ but little from the values calculated from (12), which may be considered to be very accurate; since the values of B on which they are based (see Table III) have been calculated directly from the *observed* values of D_2 according to Comm. 172*b*, and therefore refer to the saturation line.

The deviations from the law of BOYLE are comparatively great, and negligible only up to 0°.7. Above this pv_2 may no longer be put equal to RT. The same applies to v_2-v_1 (see § 3), for which v_2 may be put only to 0°.9. For benzene the deviation from the law of BOYLE at 70° ($m = 0,61$) is 2 % (Zustandsgl. p. 156); this already amounting to almost 15 % for Helium at the same reduced temperature ($T = 3°.2$)! This is

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[1] This value is no longer valid on the saturation line, as the critical volume can no longer be considered as large. Terms should then still be added with $C : v_2^2$ etc. From $B = (RT_k - p_k v_k) v_k$ is calculated the correct value —34.0.

[2] The B-values, used by M.; Cr.; K.O. and Sw. for the calculation of their D_2-values, viz. resp. —93.40, —98.05 and —99.87 (according to a kind communication from Dr. CROMMELIN), are much too great negative in my opinion, at least on the saturation line. But chiefly the p-values, used by the said authors, viz. resp. 71.10, 46.37 and 38.46 mm. (instead of 88.84, 61.47 and 52.89 mm., calculated according to (10), cf. also Table II*a*), are much too low. For the experimental value at 2°.24 is already 51 mm. (calculated 46.6, see Table I); the pressure at the *higher* temperature 2°.30, therefore, *cannot possibly* be = 38.46! The reason is, that the authors have used the formula of Comm. 147*b* (cf. § 1), which is quite inadmissible at these temperatures. It is chiefly these erroneous p-values, that have caused the great errors in the D_2-values calculated by them, through which e.g. 11,59 was found for $10^4 D_2$ at 2°.30 instead of 15,86, which value is almost 50% higher.

[3] Calculated from the diameter, see further.

[4] These values have been directly observed; they are in pretty good agreement with the calculated values. The following values have been calculated; the first three are still correct, but the last three are, in my opinion, entirely wrong. Comp. Note 2).

[5] Here a maximum for pv_2 at $m = T : T_k = 4.22 : 5.19 = 0.81$ is duly found. For "ordinary" substances this maximum lies at the same place: for benzene e.g. at $m = 0.80$ (Cf. Zustandsgl. p. 255, Fig. 8). It appears from Table IX, that the maximum of $W = p\,(v_2 - v_1)$ is situated at $m = 0.73$ ($T = 3°.8$), against 0.77 for benzene.

owing to the fact, that with equal m the deviations are about proportional to the *reduced pressures* $\varepsilon = p : p_k$. And since for Benzene $\varepsilon = 548 : 36486 = 0{,}015$ at $m = 0{,}61$, and for the Helium $= 231{,}4 : 1718 = 0{,}135$,

TABLE V.

T	m	$10^6 RT$	$p^{atm.}$	$10^6 B$	$10^6 v_2$	$10^4 D_2$	$10^6 pv_2$	△ BOYLE (%) $(RT-pv_2) : RT \times 100$
0	0	0	0	∞	∞	0	0	0
0.5	0.09634	1831	$0.0_7 2934$	—442	6241.10^7	$0.0_4 29$	1831	$0.0_3 39$
0.6	0.1156	2197	$0.0_6 58\overline{25}$	—299	3772.10^6	$0.0_3 47$	2197	$0.0_2 36$
0.7	0.1349	2563	$0.0^5 49\overline{95}$	—226	5131.10^5	$0.0_2 3\overline{5}$	2563	0.017
0.8	0.1541	2929	$0.0_4 2533$	—183	1156.10^5	0.015	2927	$0.05\overline{5}$
0.9	0.1734	3296	$0.0_4 9053$	—155	3636.10^4	0.049	3292	0.13
1.0	0.1927	3662	$0.0_3 2532$	—136	1443.10^4	0.12	3653	0.26
1.1	0.2119	4028	$0.0_3 5928$	—122	6764.10^3	0.26	4010	$0.4\overline{5}$
1.2	0.2312	4394	$0.0_2 1214$	—111	3595.10^3	0.50	4363	0.70
1.3	$0.25\overline{05}$	4760	$0.0_2 2242$	—103	2101.10^3	0.85	4711	1.03
1.4	0.2698	5127	$0.0_2 3822$	—96.0	1322.10^3	$1.3\overline{5}$	5054	1.42
1.5	0.2890	5493	$0.0_2 6107$	—90.4	8827.10^2	2.02	5391	1.86
1.6	0.3083	5859	$0.0_2 9255$	—85.7	6180.10^2	2.89	5721	2.37
1.7	0.3276	6225	0.01343	—81.8	4500.10^2	3.97	6043	2.92
1.8	0.3468	6591	0.01883	—78.4	3377.10^2	5.28	6359	3.52
1.9	0.3661	6957	0.02557	—75.4	2608.10^2	6.84	6668	4.16
2.0	0.3854	7324	0.03386	—72.8	2059.10^2	8.67	6970	4.83
2.1	0.4046	7690	0.04384	—70.4	1657.10^2	10.77	7264	5.54
2.2	0.4239	8056	0.05570	—68.3	1356.10^2	13.16	7552	6.26
2.3	0.4432	8422	0.06959	—66.5	1125.10^2	15.86	7830	7.03
2.4	0.4624	8788	0.08572	—64.8	9452.10	18.88	8102	7.81
2.5	0.4817	9155	0.1043	—63.2	8022.10	22.24	8367	8.61
2.6	0.5010	9521	0.1253	—61.8	6882.10	25.93	8623	9.43
2.7	0.5202	9887	0.1492	—60.5	5944.10	30.02	8869	10.3
2.8	$0.539\overline{5}$	10253	0.1761	—59,3	5172.10	34.50	9108	11.2
2.9	0.5588	10619	0.2059	—58.1	4535.10	39.35	9338	12.1

which is 9 times greater, the $7^1/_2$ times greater deviation for Helium is accounted for.

TABLE V *(Continued).*

T	m	$10^6 RT$	$p_{\text{atm.}}$	$16^6 B$	$10^6 v_2$	$10^4 D_2$	$10^6 pv_2$	Δ BOYLE (%) $(RT-pv_2):$ $: RT \times 100$
3.0	0.5780	10985	0.2392	—57,0	3997.10	44.64	9561	13.0
3.1	0.5973	11352	0.2761	—56.0	3545.10	50.34	9772	13.9
3.2	0.6166	11718	0.3167	—55.1	3147.10	56.70	9967	14.9
3.3	0.6358	12084	0.3614	—54,2	2810.10	63.50	1016.10	16.0
3.4	0.6551	12450	0.410$\overline{5}$	—53.4	2516.10	70.92	1033.10	17.0
3.5	0.6744	12816	0.4639	—52.6	2261.10	78.92	1049.10	18.2
3.6	0.6936	13182	0.5230	—51.8	2034.10	87.73	1064.10	19.3
3.7	0.7129	13549	0.5872	—51.1	1833.10	97.35	1076.10	20.6
3.8	0.7322	13914	0.6567	—50.4	1655.10	107.8	1087.10	21.9
3.9	0.751$\overline{5}$	14281	0.7316	—49.7	1499.10	119.0	1097.10	23.2
4.0	0.7707	14647	0.8121	—49.1	1359.10	131.3	1104.10	24.7
4.1	0.7900	15013	0.8991	—48.5	1232.10	144.8	1108.10	26.2
4.2	0.8093	15380	0.9918	—47.9	1119.10	159.$\overline{5}$	1111.10	27.8
4.3	0.8285	15746	1.090	—47.3	1019.10 (1021.10)	175.1 (174.8)	**1112.10**	29.4
4.4	0.8478	16112	1.194	—46.8	9271 (9298)	192.$\overline{5}$ (191.9)	1109.10	31.2
4.5	0.8671	16478	1.30$\overline{5}$	—46.2	842$\overline{5}$ (8461)	211.8 (210.9)	1102.10	33.1
4.6	0.8863	16844	1.421	—45.7	7649 (7658)	233.3 (233.0)	1088.10	35.4
4.7	0.9056	17210	1.546	—45.2	6887 (6878)	259.1 (259.4)	1064.10	38.2
4.8	0.9249	17577	1.676	(—44.7)	6108	292.1	1024.10	41.8
4.9	0.9441	17943	1.816	(—44.2)	5340	334.1	9697	46.0
5.0	0.9634	18308	1.961	(—43.8)	4564	391.0	8950	51.1
5.1	0.9827	18675	2.116	(—43.3)	3744	476.6	7922	57.6
5.19	1	1900$\overline{5}$	2.261	(—42.9)	2572	693.8	5815	69.4

From $pv_2 = RT + \frac{B}{v_2}$ follows $\Delta = (RT - pv_2) : RT = -\frac{B}{v_2} : RT$. And B being $= RTb_g - a_g$ for large volumes, Δ becomes $= (a_g - RTb_g) : RTv_2$, in which a_g and b_g are the values of a and b at the temperature T

and at $v = \infty$. As a is practically independent of the volume, a may simply be written instead of a_g. Now at lower temperatures $\lesssim a_k$ may be substituted for $a - RTb_g = \theta a_k - RTb_g$ (in which for ordinary substances θ is always > 1, but for Helium < 1); hence we get ($m = T : T_k$):

$$\triangle \lesssim \frac{a_k}{RTv_2} \lesssim \frac{a_k \cdot p}{RT \cdot pv_2} \lesssim \frac{a_k \cdot p}{(RT)^2} \lesssim \frac{a_k \cdot \varepsilon p_k}{m^2\,(RT_k)^2}.$$

With $p_k = \frac{1}{27}\frac{a_k}{b_k^2}$, $RT_k = \frac{8}{27}\frac{a_k}{b_k}$ this becomes:

$$\triangle \lesssim \frac{27}{64}\frac{\varepsilon}{m^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

From this follows, therefore, that with equal m, $\triangle$ is "about" proportional to ε. With his usual lack of thoroughness NERNST writes simply ε for $[RT - p(v_2 - v_1)] : RT$, which does not differ much from $\triangle$ up to near T_k. This is only correct in approximation at $m^2 = {}^{27}/_{64}$, $m = 0{,}63$, but of course not with arbitrary values of m. How great the differences, accordingly, are between NERNST and reality, especially at higher reduced temperatures, appears from the table on p. 257 of my "Zustandsgleichung".

Let us take as example Helium at $m = 0{,}5$ ($T = 2^\circ{,}6$). Here ε is $= 0{,}1253 : 2{,}261 = 0{,}0554$, so that $\triangle$ is somewhat $< \frac{27}{64} \times 0{,}2216$, or $< 0{,}109$. We really found $9{,}43\,^0/_0$, i.e. $0{,}094$.

The explanation, why ε for Helium is e.g. 9 times greater than for benzene at the same value of m (see above), follows from the approximated vapour pressure formula $-\log \varepsilon = f\left(\frac{1}{m} - 1\right)$ or $\varepsilon = e^{-f\left(\frac{1}{m}-1\right)}$. Now $f = 3.16$ for Helium at $m = 0{,}61$, and $f = 6{,}59$ for benzene [1], so that ε becomes resp. $= e^{-2{,}02}$ and $e^{-4{,}20}$, i.e. for Helium $e^{2{,}18} = 8{,}8 = 9$ times greater than for benzene.

The same ratios are found for $v_2 : v_1$ (see Table IX). Thus e.g. $v_2 : v_1$ is only $= 23$ for Helium ($3^\circ{,}26$) at $m = 0{,}63$, this ratio being 300 at the boiling-point (80° C.) of benzene (m likewise $= 0{,}63$).

3. The values of $^1/_2\,(D_1 + D_2)$ and $^1/_2\,(D_1 - D_2)$ in the neighbourhood of the critical temperature.

For the calculations of the so-called "Diameter" we only use those data, that are sufficiently far from the maximum liquid density at $2^\circ{,}3$; we take the following values of D_1 and D_2 (see also Table IV).

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[1] This depends again on the family of the substances, as $f \sim 8\gamma$, and γ is $= 0.9$ or 1 for ordinary substances and <0.5 for Helium.

TABLE VI.

T	D_1 (C.172^b)	$D_{2\,\mathrm{calc.}}$ (Table IV)	$^1/_2\,(D_1+D_2)$	Ibid formula
*3.30	0.1395	0.0063^5	0.0729^{25}	0.0729^{25}
*3.90	0.1311	0.0119^0	0.0715^0	0.0715^0
4.22	0.1255	0.0162^5	0.0708^{75}	0.0708^{54}
*4.23	0.1253	0.0163^7	0.0708^{35}	0.0708^{35}
4.59	0.1165	0.0230^6	0.0697^8	0.0702^{06}
4.71	0.1139	0.0262^4	0.0700^7	0.0700^{18}

From the values at 3°,30, 3°,90 and 4°,23, marked by us with an asterisk, we calculate:

$$10^4\,.\,{}^1/_2\,(D_1+D_2)=857{,}41-51{,}60\,T+3{,}868\,T^2,$$

which, accordingly, gives a course *convex* towards the T-axis (*concave* at lower temperatures, where D_1 quite predominates with its maximum). We may also write:

$$\underline{10^4\,.\,{}^1/_2\,(D_1+D_2)=693{,}79+11{,}45\,(T_k-T)+3{,}868\,(T_k-T)^2,}\qquad(15)$$

or also with $T=mT_k$:

$$10^4\,.\,{}^1/_2\,(D_1+D_2)=693{,}79+59{,}426\,(1-m)+104{,}19\,(1-m)^2,$$

or with $D=d\times D_k$, in which d is, therefore, the reduced density:

$$\underline{{}^1/_2\,(d_1+d_2)=1+0{,}085654\,(1-m)+0{,}15017\,(1-m)^2.}$$

From this follows:

$$\gamma=0{,}085654+0{,}30034\,(1-m),$$

which, at T_k $(m=1)$ gives $\gamma=0{,}086$, but at $T=3°{,}90$ $(m=0{,}75)$ already $0{,}86+0{,}075=0{,}161$, i.e. almost *double* the value!

We find for D_k:

$$\underline{10^4\,D_k=693{,}8.}\quad(\text{Comm. }172b:\ 693{,}0).$$

If the values, found for $^1/_2\,(D_1+D_2)$ according to the formula, are assumed to be correct, and also the calculated values of D_2, the value $1254^6=1255$ (exp. 1255), follows for $10^4\,D_1$ at 4°,22, the value $1173^{52}=1174$ (exp. 1165) at 4°,59, and the value $1137^{96}=1138$ (exp. 1139) at 4°,71. Accordingly it follows that there is no objection to calculating D_2 to 4°,7 from the values of B and p calculated by us, which we, accordingly, have done in Table V. The corresponding values of D_1 between 3°,3 and 4°,7 can then be calculated from (15).

Past $4^{\circ},71$ up to $5^{\circ},19$ recourse must be had to a theoretical formula for $^1/_2\,(D_1-D_2)$, valid in the neighbourhood of T_k, viz. (cf. also Zustandsgl. p. 332 and 346)

$$\frac{^1/_2\,(D_1-D_2)}{\sqrt{T_k-T}}=\alpha'-\beta'\,(T_k-T)+\delta'\,(T_k-T)^2\ldots$$

For the calculation of the coefficients α', β' and δ' we use the following data.

TABLE VI^a.

T	D_1	D_2	D_1-D_2	$\sqrt{T_k-T}$	$^1/_2\,(D_1-D_2):\sqrt{\ }$
4.23	0.1253	0.0163^7	0.1089^3	0.9798	555.9
4.59	0.1173^5	0.0230^6	0.0942^9	0.7746	608.6
4.71	0.1138	0.0262^4	0.0875^6	0.6928	631.9

And from this follows:

$$^1/_2(D_1-D_2):\sqrt{T_k-T}=753.77-301,67\,(T_k-T)+99,54\,(T_k-T)^2, \quad (16)$$

for which may also be written, with $D=d\times D_k$:

$$^1/_2(d_1-d_2):\sqrt{T_k-T}=1,086\bar{5}-0,43481\,(T_k-T)+0,14347\,(T_k-T)^2$$
$$=1,086\bar{5}-2,2567\,(1-m)+3,8645\,(1-m)^2,$$

hence

$$^1/_2\,(d_1-d_2):\sqrt{1-m}=2,475-5,141\,(1-m)+8,804\,(1-m)^2.$$

The constant term a is therefore $=2,475$. This is 3,6 to 4 for ordinary substances ($\gamma=0,9$ to 1), about 3 for argon ($\gamma=0,75$) and 2 for "ideal" substances (a and b constant, $\gamma=0.5$). Hence a is always — 4γ.

Now for Helium $s=R\,T_k:p_k v_k=0,019005:0,005815=3,268$ (see Table V), and s being $=8\,\gamma:(1+\gamma)$, the value 0,69 would follow for the "theoretic" value of γ for Helium, so that $4\,\gamma$ becomes $=2,76$, which is, therefore, here slightly more than 2,475. For the quantity $r=v_k:b_k$ we find for Helium $0,002572:0,001051=2,447$. For rs we find for Helium the general value 8, as $3,268\times 2,447=7,997=8,00$. (Compare also Zustandsgl. p. 141). [For "ideal" substances s is $={}^8/_3$ and r is $=3$; for ordinary substances s is $=3,6$ to 4, r is $=2,22$ to 2].

From (15) and (16) the following values are now calculated between $4^{\circ},3$ and $5^{\circ},2$; those of D_2 and v_2 have already been recorded in Table V.

As regards D_1, we have already the values between $4^{\circ},3$ and $5^{\circ},19$ in the following Table. Further we have the experimental material of Comm. 170 (K. ONNES and BOKS) and 172*b* (M., CR., K.O. and SW.) between $1^{\circ},2$ and $4^{\circ},2$ (Table VIII), and also the values calculated by us in Table A of the first Part of this paper.

TABLE VII.

T	$10^4 \cdot {}^1\!/_2 (D_1+D_2)$	$10^4 \cdot {}^1\!/_2 (D_1-D_2)$	$10^4 D_1$	$10^4 D_2$	$10^6 v_1$	$10^6 v_2$
4.3	707.0	532.2	1239	174.8	1440	10206
4.4	705.2	513.3	1219	191.9	1464	9298
4.5	703.5	492.6	1196	210.9	1492	8461
4.6	701.9	468.9	1171	233.0	1524	7658
4.7	700.3	440.9	1141	259.4	1564	6878
4.8	698.8	406.7	1106	292.1	1614	6108
4.9	697.4	363.3	1061	334.1	1682	5340
5.0	696.1	305.1	1001	391.0	1782	4564
5.1	$694.\overline{9}$	218.2+	913.1	476.6	1954	3744
5.19	693.8	0	693.8	693.8	2572	2572

The values of D_1 according to Comm. 170 and 172*b* are the following. Those of Comm. 170 have all been increased by 7 units of the last decimal, in accordance with the last correction in Comm. 172*b* on account of an improved determination of the normal volume.

TABLE VIII.

T	$10^4 D_1$	T	$10^4 D_1$	T	$10^4 D_1$
1.20	1459	2.10	1464^5	2.56	1457
1.28	1459	2.21	1466	3.30	1395
1.59	1460	2.30	**1496** (max)	3.90	1311
1.92	1462	2.37	1466	4.22	1255
1.93	1462				

From this, interpolations can easily be made from 1°,2 to 3°,3. But between 3°,3 and 4°,2 some D_1-values must still be calculated. This is done by substracting the values of D_2 from the values of $D_1 + D_2$ calculated according (15), through which the following table is obtained.

TABLE VIII^a^.

T	$10^4 (D_1+D_2)$	$10^4 D_2$	$10^4 D_1$	T	$10^4 (D_1+D_2)$	$10^4 D_2$	$10^4 D_1$
3.3	1458.5	63.5	1395	3.8	1434.4	107.8	1327
3.4	1453.4	70.9	1382	3.9	1430.0	119.0	1311
3.5	1448.4	78.9	1369	4.0	1425.8	131.3	1294
3.6	1443.6	87.7	1356	4.1	1421.7	144.8	1277
3.7	1438.9	97.4	1342	4.2	1417.8	159.5	1258

4. The values of $W = p\,(v_2 - v_1)$, L and λ.

Now the whole material is complete for the determination of W (the values of p in atm. should be taken from Table V), $L = F \times W$, and

TABLE IX.

T	$10^4 D_2$	$10^4 D_1$	$10^6 v_2$	$10^6 v_1$	$v_2 : v_1$	$10^6 W = 10^6 . p\,(v_2 - v_1)$	F	$10^5 L$ (norm. units)	L' (Gr. cal.)	$10^5 \lambda = L - W$ (norm. units)
0	0	1458^6	∞	1223^4	∞	0	∞	3230	17.53	3230
0.5	$0.0_4 29$	**1458^0** (min)	6241.10^7	**1223^9** (max)	5.10^7	1831	17.88	3274	17.77	3091
0.6	$0.0_3 47$	1458^1	3772.10^6	1223^9	3.10^6	2197	14.99	3293	17.87	3073
0.7	$0.0_2 \overline{35}$	1458^1	5131.10^5	1223^8	4.10^5	2563	12.94	3317	18.00	3061
0.8	0.015	1458^2	1156.10^5	1223^7	1.10^5	2927	11.41	3340	18.12	3047
0.9	0.049	1458^3	3636.10^4	1223^6	3.10^4	3292	10.24	3371	18.29	3042
1.0	0.12	1458^5	1443.10^4	$1223^{\bar{5}}$	12.10^3	3652	9.306	3399	18.44	3034
1.1	0.26	1458^7	6764.10^4	1223^3	55.10^2	4009	8.553	3429	18.61	3028
1.2	0.50	1459^0	3595.10^3	1223^1	29.10^2	4362	7.933	3459	18.77	3023
1.3	$0.\overline{85}$	1459^3	2101.10^3	1222^8	172.10	4708	7.416	3491	$18.\overline{95}$	3021
1.4	1.3	1459^6	1322.10^3	1222^5	108.10	5049	6.980	3524	19.12	3019
1.5	2.0	1460^0	8827.10^2	1222^2	722	5384	6.608	3558	19.31	**3019** (min)
1.6	2.9	1460^5	6180.10^2	1221^8	506	5710	6.289	3591	19.49	3020
1.7	4.0	1460^9	4500.10^2	1221^4	369	6027	6.013	3624	19.67	3021
1.8	5.3	1461^4	3377.10^2	1221^0	277	6336	5.774	3658	19.85	3022
1.9	6.8	1462^0	2608.10^2	1220^5	214	6637	5.564	3693	20.04	3029
2.0	8.7	1563^0	2059.10^2	1219^7	169	6929	5.381	3728	20.23	3035
2.1	11	1464	1657.12^2	1219	136	7211	5.219	3763	20.42	3042
2.2	13	1466	1357.10^2	1217	111	7484	5.077	3800	20.60	**3052** (point of inflection)
2.3	16	**1469** (max)	1125.10^2	**$12\overline{15}$** (min)	93	7744	4.951	**3834** (point of inflection)	**20.80**	3060
2.4	19	1465	9452.10	1218	78	7998	4.840	3871	21.01	3071
2.5	22	1460	8022.10	1222	66	8239	4.741	3906	21.20	3082
2.6	26	1454	6882.10	1227	56	8469	4.654	3941	21.39	3094
2.7	30	1448	5944.10	1232	48	8685	4.577	3975	21.57	3107
2.8	34^5	1442	5172.10	1237	42	8890	4.509	4009	21.75	3120
2.9	39	1435	4535.10	1244	36	9081	4.449	4040	21.92	3132

TABLE IX (*Continued*).

T	$10^4 D_2$	$10^4 D_1$	$10^6 v_2$	$10^6 v_1$	$v_2 : v_1$	$10^6\,W = 10^6 \,.\, p\,(v_2 - v_1)$	F	$10^5\,L$ (norm. units)	L' (Gr. cal.)	$10^5\,\lambda = L - W$ (norm. units)
3.0	$4\bar{5}$	1427	3997.10	1250	32	9262	4.396	4072	22.09	3146
3.1	50	1418	3545.10	1258	28	9440	4.349	4105	22.28	3161
3.2	57	1407	3147.10	1268	25	9565	4.309	4122	22.36	3165
3.3	63^5	1395	2810.10	1279	22	9693	4.274	4143	22.48	3174
3.4	71	1382	2516.10	1291	19	9798	4.242	4156	22.55	**3176** (max)
3.5	79	1369	2261.10	1303	17	9884	4.212	**4163** (max)	**22.59**	3175
3.6	88	1356	2034.10	1316	15	9950	4.183	4162	22.58	3167
3.7	97	1342	1833.10	1320	14	9982	4.154	4147	22.50	3149
3.8	108	1327	1655.10	1345	12	**9985** (max)	4.125	4119	$22.3\bar{5}$	3120
3.9	119	1311	1499.10	1361	11	9971	4.096	4084	22.16	3087
4.0	131	1294	1359.10	1379	10	9917	4.067	4033	21.89	3041
4.1	$14\bar{5}$	1277	1232.10	1397	8.8	9821	4.038	3966	21.52	2984
4.2	159^5	1258	1119.10	1418	7.9	9692	4.009	3886	21.08	2917
4.3	175	1239	1020.10	1440	7.1	9559	3.980	3804	20.64	2848
4.4	192	1219	9284	1464	6.4	9337	3.952	3697	20.06	2762
4.5	211	1196	8443	1492	5.7	9071	3.925	3570	19.37	2661
4.6	233	1171	7654	1524	5.0	8711	3.900	3399	$18.4\bar{5}$	2527
4.7	259	1141	6882	1564	4.4	8222	3.877	$318\bar{5}$	17.28	2363
4.8	292	1106	6108	1614	3.8	7532	3.857	2905	15.76	2152
4.9	334	1061	5340	1682	3.2	6643	3.839	2550	13.84	1886
5.0	391	1001	4564	1782	2.6	5456	3.822	2085	11.32	1539
5.1	477	913	3744	1954	1.9	3788	3.808	1442	7.83	1063
5.19	694	694	2572	2572	1	0	$3.79\bar{5}$	0	0	0

$\lambda = L - W$ (see (11) in § 1). The values of D_2 and v_2, already given in Table V, have been repeated in the foregoing Table IX, as also the values of F from Table II. To reduce L expressed in normal units to L' in gr. cal., we must multiply by 542,63 (see § 2 of the first Part of this paper).

When we represent the values, found for L in this table — which, as appears from what precedes, have been calculated with the greatest care and accuracy from the available data concerning p, B, D_2 and D_1 — by a graph, we obtain a continuous curve, which has a *maximum* at 3°,5, and a *point of inflection* at 2°,3. The presence of this point had already been stated in § 4 of the first Part. The maximum had necessarily to appear, because the initial course at $T=0$ is *ascending*. (cf. there formula (9)).

On the contrary the initial course of λ is *descending* (loc. cit.), and leads necessarily to a *minimum* (at about 1°,5), because λ in conformity with L has a *maximum* at almost the same place (3°,4). Of course there is again a *point of inflection* between minimum and maximum, and this about at the same temperature as that of the point of inflection of L (c.f. Fig. 2).

DANA and KAMERLINGH ONNES (loc. cit., cf. § 1 of the first Part) also made a calculation of the values of L between 3° and 5°, but in consequence of the less accurate values of $dp/_{dt}$ and $v_2—v_1$, used by them, they only obtained a rough approximation (see the following table). They find, indeed, also the maximum at 3°,5, but their values at 3°, 3°,5 and 4° are slightly too high. That at 5° is almost identical with ours, the value at 4°,5, viz. 16,0, being quite incongruous. In their graphic representation they have, accordingly, substituted 19 (i.e. 4,75 gr. cal. per gr. He) for this value (i. e. 4 gr. kal. per gr. He), through which they have obtained a continuous curve (loc. cit. p. 1056).

The values found experimentally by DANA and K.O. are, indeed, in harmony, as far as order of magnitude is concerned (see Table X), with our calculated values; but the place of the maximum can hardly be ascertained from them, since their values are about constant between 2° and 3°,5.

TABLE X.

	$T=0$	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.19
$L_{theor.}$ v. L. =	17.5	17.8	18.4	19.3	20.2	21.2	22.1	**22.6**	21.9	19.4	11.3	0
Ibid. D.; K.O.	—	—	—	—	—	—	23.2	24	22.8	(16.0?)	11.2	0
$L_{exp.}$ „	—	—	—	21.8	22.3	22.4	22.6	22.2	20.2	—	—	—

More accurate measurements will be required to establish the course experimentally with more certainty. From their measurements the authors also conclude (see the footnote on p. 1057), that there happens "*something particular*" in the neighbourhood of 2°,3 (which happens to be exactly the place of the maximum liquid-density). But the degree of accuracy of their experiments does not allow them here either to elucidate this point further. But after our considerations and calculations we now know, that really something particular happens here, i. e. the occurrence of a *point of inflection*, below which the course of L is *convex* with regard to the temperature-axis, and above which it becomes *concave*, proceeding to the maximum at 3°,5.

As we have seen, the appearance of this maximum can be explained in a *perfectly natural* way, of which the clue lies in formula (9), viz. (augmented by R, to transform $d\lambda/dt$ to dL/dt)

$$\frac{dL}{dt}=-\frac{\beta a_0}{v_0^2}+R=-0{,}003127+0{,}003662=+0{,}000535,$$

through which, owing to the abnormally low value of a_0 for Helium, dL/dt proves to be *positive*, instead of negative, as in all other substances. Consequently the appearance of this maximum does not give in my opinion — in opposition to DANA and K. O.'s opinion — the slightest support to the calculations of VERSCHAFFELT cited in their paper, which are in connection with a possible "degeneration of energy" of the liquid at very low temperatures. The degeneration of energy is, in my opinion, not only *improbable* (it does not even explain the maximum and minimum in the liquid density), but its assumption is also *unnecessary*, because the ordinary theory, taking the deviating behaviour of the quantity a into consideration (rise instead of fall on increasing temperature), accounts for all the particularities, even in detail.

Also the abnormally low specific heat, but this will be treated on a subsequent occasion.

Tavel sur Clarens, Suisse, Summer 1926.

Physiology. — *"Veratrine poisoning of degenerated mammalian muscle."* By ARIE QUERIDO. (Communicated by Prof. G. VAN RIJNBERK.)

(Communicated at the meeting of October 30, 1926).

An investigation into the action of veratrine on degenerated muscle will give the opportunity to throw some light on two till now unsolved difficulties in the problem of the action of veratrine on skeletal muscle. The structure of muscle changes in a definite and well-known way during degeneration; if we find that veratrine has on degenerated muscle an effect different from the normal, we may be able to demonstrate a causal relation between the changed structure and the change in function. Furthermore, severance of the motor innervation is the only method possible to obtain a muscle free from nervous elements; in this way we may study the action of veratrine on striated muscle without poisoning simultanously any nerve fibres.

As far as I know, the previous work on this subject consists of two publications only, both by FONTÈS [1]). He cut the sciatic nerve in frogs and poisoned after a varying interval their muscles. The contraction, obtained from the M. Gastrocnemius had the typical shape we also find in the intact muscle after veratrine poisoning.

FONTÈS made his investigation in winter; the longest interval between the section of the nerve and the poisoning of the muscle was three months. This is certainly not long enough for a frog's muscle to degenerate. I cut in some frogs the sciatic in November, and was not able to find any indication of degeneration in the muscles on the operated side in April [2]).

Therefore it is probable that FONTÈS worked on non-degenerated muscles; the conclusions drawn by him from his experiments are not justified; I repeated the procedure, but with warm-blooded animals.

In aether narcosis under aseptic precautions I cut the N. Ischiadicus in a number of albino-mice on the left side.

The muscles of the hind legs of those animals were tested with intervals of one day, the first 24 hours after operation.

The animals were anaesthetised with urethane (1 cc. of a 10 % solution, injected intra-peritonally per 100 Gr. mouse). I freeed the cut end of the sciatic from surrounding tissue and cut the sciatic on the other side; both tendons of Achilles were cut loose from their insertion and connected with a writing lever, providing a load of 3 Gr. The sciatic nerves were placed on a pair of stimulating electrodes; in both the Gastrocnemic muscles a pair of silver needle-electrodes were thrusted. Three double-throw double-pole switches allowed a rapid change from faradic to galvanic stimulation,

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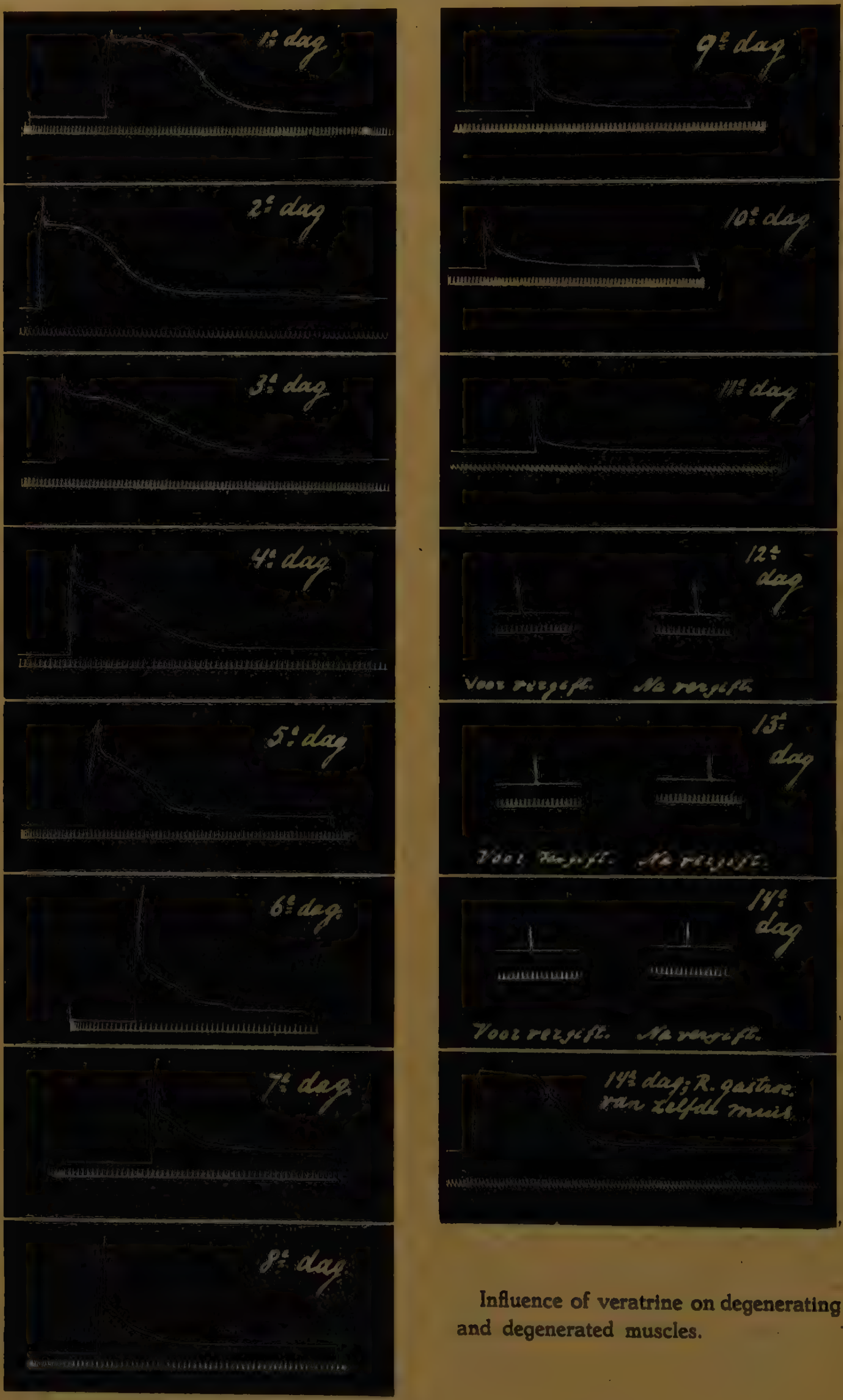
[1]) Comptes-rendus Soc. Biol. 1921, LXVI, 84; Journ. de Physiol. et de Pathol. gén. 1925, XXIII, 292.

[2]) Cf. BREMER and GERARD, Comptes-rendus Soc. belge de Biol. 1926, XCIV, 1035.



Influence of veratrine on degenerating and degenerated muscles.

from direct to indirect stimulation, and made it possible to stimulate right or left without disturbing the preparation. Faradic stimuli were provided by a DUBOIS—REYMOND induction coil, the strength of stimulus being varied by changing the resistance of the primary circuit; in the table the strength of stimulus is expressed by the size of the primary current which is direct proportional to this value. In wiring the set-up care had been taken that one electrode acts as cathode on the break, both of induction shocks and of constant current; this electrode was always distal to its fellow.

When the narcotised mouse had been prepared as described above, I first compared the threshold for indirect stimuli right and left; after this the threshold for direct stimuli right and left was compared, and thereupon the behaviour of both muscles in regard to constant current.

In this way a complete insight was obtained into the stage of degeneration of the left Gastrocnemic of the tested mouse. Now I injected into both muscles 0.1 cc. veratrine solution 1 : 20.000, and compared after 3 minutes the contraction right and left on direct stimulation with induction shocks.

No clear differences are found in the first three days following the operation; after this time the differences are unmistakable. The second part of the contraction of the muscle on the operated side takes less time and is lower; small oscillations are superponed on the second part of the contraction curve. Day after day the points of difference between the contractions right and left become more distinct; the characteristic shape of the veratrine contraction dissappears quite gradually in the curve from the muscle on the operated side. Twelve days after the operation we find after poisoning a contraction that is in all aspects similar to the contraction of the same muscle before poisoning. No indication of an influence of the drug can be found in the shape of the shortening curve.

We may follow the process of degeneration until the musle has lost its direct irritability — eight weeks after section of the nerve — and during this period the effect of veratrine on the degenerated muscle does not change, and remains nil.

We observe that the first muscle that does not show any typical effect of the poisoning is the same to show a complete electrical reaction of degeneration (Vide Table). From the twelfth day following the section of the nerve the chief points of electrical degeneration are regularly present. and from this day on no difference can be found between the contraction before and after poisoning on the operated side.

Microscopic examination. BIELSCHOWSKY-preparations, made by Dr. H. C. VOORHOEVE from the tested muscles, showed, that 14 days after the section of the nerve no motor end-organs were to be found in the muscles. But in those muscles, and à fortiori in muscles that were examined at a shorter interval after operation, no difference could be detected in the structure (aspect of striation, number and distribution of nuclei, amount of sarcoplasma) compared with normal muscle.

TABLE.

Development and progress of degeneration on the operated side.

Day	Strength of current milli-Amps, used for stimulation of nerve and muscle.						
	Faradic		Galvanic				
	Nerve	Muscle	Cath. make	Anod. break	Anod. make	Cath. tetan.	Cath. break
1	0.5	0.8	2.0	3.2	5.5	10.4	22
2	0.8	1.1	1.8	3.0	4.8	12.2	22
3	0.8	1.2	2.2	3.5	5.0	12.0	20
4	1.3	1.5	2.5	4.0	4.2	12.0	21
5	1.3	1.8	2.5	3.8	4.5	10.8	18
6	2.0	1.3	2.7	4.1	4.5	10.6	18
7	2.2	2.8	3.1	5.0	4.0	12.4	19
8	3.5	3.5	3.5	5.2	4.0	11.3	22.5
9	3.4	3.7	3.8	5.4	3.8	12.0	22
10	4.6	4.0	4.0	5.5	3.8	10.5	22
11	5.7	4.0	4.5	6.0	4.1	12.2	24
12	—	4.2	6.0	7.4	5.0	11.6	22.5
13	—	4.2	5.1	9.0	4.8	8.2	18
14	—	4.5	5.4	6.8	6.0	9.4	21
15	—	6.0	5.4	7.2	4.8	10.2	15
16	—	5.5	7.0	8.5	6.2	8.5	18
17	—	6.2	7.0	8.5	5.7	7.9	17

Sympathetic. When the sciatic nerve is sectioned, of course the sympathetic innervation of the Gastrocnemic muscle is interrupted at the same time.

Therefore I performed some experiments in which the spinal innervation was left intact, and only the sympathetic nerve paths were interrupted.

In a number of rats the sympathetic chain was exstirpated on the left side from the solar plexus downward.

The first of those rats was examined two weeks after the operation, the others with intervals of a fortnight after the first; the last rat twelve weeks after the operation.

Some of those animals showed a difference in temperature and in aspect of both hindlegs; one rat had a marked edema of the left hindleg and foot.

The contractions obtained from the Mm. Gastrocnemii did not show any difference before nor after poisoning between the muscles from the operated and from the intact side.

Conclusions. Muscles that are caused to degenerate by cutting their motor nerve show gradually a diminishing influence of veratrine poisoning.

From muscles that are completely degenerated as shown by electrical test, a veratrine contraction cannot be elicited; after poisoning they yield on induction shock a single muscle twitch, just as before poisoning.

This is also true for muscle that do not show any structural change when examined microscopically.

Muscles, lacking sympathetic innervation, yield veratrine contractions that are identical to those of intact muscles after poisoning.

Physiology. — *"Veratrine contraction of the frog's heart."* By ARIE QUERIDO. (Communicated by Prof. G. VAN RIJNBERK.)

(Communicated at the meeting of October 30, 1926).

The function of the heart of a cold- or warm-blooded animal will be changed profoundly when the animal has been poisoned by veratrine.

Those changes have a twofold character: the rhythm of the pulsations is affected — it becomes irregular, more frequent at first, to slow down afterwards, and the coordination between the subdivisions of the heart is impaired — as the poisoning progresses, a partial heartblock becomes more and more apparent.

The activity of the heart muscle as indicated by the shape of each contraction is influenced only quantitatively, in accordance to the changes of the rhythm in wich the pulsations follow each other; the character of each contraction however is similar to that of the non-poisoned organ, contrary to the conduct of the skeletal muscle after poisoning. When we bear in mind that a poisoned skeletal muscle which is stimulated at a sufficient rapid rate will yield contractions that are identical to normal twitches, and that the heart muscle is under analogous conditions as a frequently stimulated skeletal muscle, it is clear that we cannot expect a functioning heart to yield veratrine contractions.

In order to obtain this result it will be necessary to suspend for a period the normal activity of the heart.

The faradisation of the Nervus Vagus seems to be the simplest way to reach this. BUSQUET and PACHON [1]) have demonstrated that veratrine poisoning of an animal results in loss of influence of the Vagus on the activity of the heart.

This is true only, if veratrine be applied on the heart in a concentration higher than 1 : 100.000. If more diluted solutions are used the heart will still stop on vagal stimulation, at least in the first minutes following the application of the drug. I have studied the nature of the reaction on an extra stimulus, when the heart has been poisoned previously by a slight dose of veratrine and has been stopped by faradisation of the N. Vagus.

Method. The brain of a large-sized frog is destroyed by a needle introduced in the median line behind the acustic membranes. The animal is pinned on the back, and the heart is exposed by removing a part of the sternum and opening the pericard. I connect the apex of the ventricle with a light writing lever, and at one side (which is irrelevant) I expose the N. Vagus by means of a partial resection of the lower jaw; the nerve is cut, and its peripheral end is placed on a pair of stimulating electrodes, connected with the secundary of an induction coil. After ascertaining that faradisation of the Vagus causes the heart to stop, I inject into the peritoneal cavity 1 cc. of a veratrine solution 1 : 10.000. While the movements of the heart are being registrated on the smoked drum, faradic stimuli are applied on the N. Vagus; the heart stops; after a few seconds, I touch the ventricle lightly with a glass rod which is drawn out into a fine point. Faradisation of the Vagus is continued until the contraction set up by the contact has come to end.

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[1]) Comptes-rendus Soc. Biol. 1906, LXI, 89.
Ibid. 1907, LXII, 943.

Fig. 1 shows the result of such an experiment; the last contraction of the heart before it responds to vagal stimulation and stops, shows already a peculiar lengthening; on mechanical stimulation a contraction is elicited that is undoubtedly of the veratrine type, viz. reaches a greater height than the other contractions, that is considerably prolonged, and that shows two consecutive shortenings of the muscle, the second one being the slower. When faradisation of the Vagus ceases, the heart resumes its former activity.

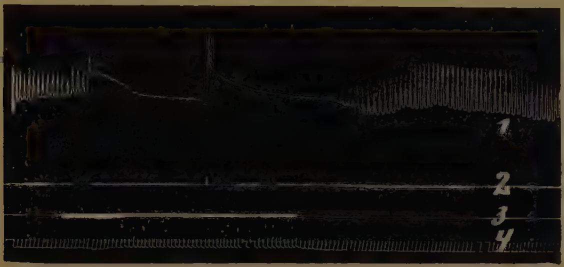

Fig. 1.
1. Suspension curve from ventricle. 2. Signal for mechanic stimulation.
3. Signal for vagal stimulation. 4. Time, 1 sec.

In those experiments we meet the difficulty that the heart sometimes „escapes" the influence of the Vagus, and contracts once or twice during the vagal stimulation; this is seen repeatedly in non-poisoned preparations, but after veratrine poisoning this tendency to escape becomes much stronger. Sometimes it appears to be impossible to force the heart to rest long enough to obtain a veratrine contraction on mechanic stimulation. The contractions may have a somewhat longer duration and may be slightly larger than their predecessors, but the differences are not clear enough. Therefore I used also another method to obtain veratrine contractions from the heart after a period of artificial rest.

A frog's heart is removed from the body and is pinned on a cork by the vessels that arise from it.

The apex of the ventricle is connected with a lever. Now I perform the so-called first ligature of STANNIUS, viz. with a silk thread the Sinus venosus is separated from the rest of the heart. This causes the heart to stop. After waiting a couple of minutes — not too long, since the heart will resume its activity after a certain interval, and the duration of this interval varies widely in the experiments — a few drops of a veratrine solution 1 : 10.000 are trickled on the heart; 2—3 minutes afterwards the heart is touched by the glass rod.

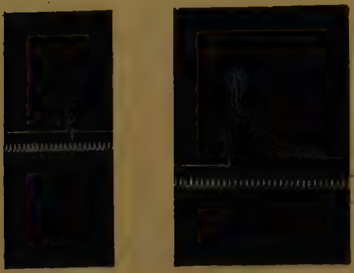

Fig. 2.

Fig. 2 shows the outcome of such an experiment; two contractions are represented, yielded by the heart after the STANNIUS ligature on mechanic stimulation, the first before, the second after veratrine poisoning. It is clear that the second curve is identical with the shortening curve of a skeletal muscle after veratrine poisoning.

The first series of experiments was repeated 18 times, the second series 26 times; the results were similar in all single cases.

When a contraction was elicited after stopping the heart and applying veratrine, this contraction always showed the shape that is characteristic for the shortening curve of veratrine-poisonend skeletal muscle.

In the cases in which stoppage of the heart was obtained by stimulating the Vagus, I have not investigated the shape of a contraction on mechanic stimulation before veratrine was applied; but in the second series of experiments this control was taken regularly, and the difference in shape of contraction curve before and after poisoning could be demonstrated in each experiment.

Conclusion. When the rhythmic activity of the frog's heart is suppressed, either by stimulating the N. Vagus or by the first ligature of STANNIUS, and the heart is poisoned by veratrine, the ventricle will give a contraction on mechanic stimulation that is identical to the contraction of a skeletal muscle after veratrine poisoning.

Botany. — *"Rapid Flowering of Darwin-tulips."* I. By Prof. A. H. BLAAUW. (Laboratory for Plantphysiol. research. Communic. N⁰. 21, Wageningen.)

(Communicated at the meeting of September 25, 1926).

§ 1. *Introductory.*

Our experiments on "the results of the temperature-treatment in summer for the Darwin-Tulips" have only been made on the red variety Pride of Haarlem. From those experiments follow various indications for culture, also for early flowering. On exposure to 44 different combinations of temperature in summer from lifting to planting (1922), it was already a striking fact for the botanist to discover that an exposure of 11 weeks to so low a temperature as 9°, gives the earliest bloom the next spring (1923). (See N⁰. 17, Tab. 2 and fig. 2.)

Meanwhile exposures to other combinations occurred, described in N⁰. 19; the question was a.o. whether more rapid flowering might be obtained in another way than by a permanent exposure to 9° in summer. Not that this could be of economical interest for field-cultures, but it might give an indication with respect to earliest bloom. Moreover on permanent exposure to 9° those flowers, though early, were rather frequently irregular or crooked, on account of transitional forms between the upper foliage-leaf and the first tepal. If we compare the number of temperature-combinations tried in 1924, among which 21 which had not yet been applied in 1922, we see in table 14, last column, that the tulips exposed to 9° for 11 weeks in summer, and those exposed to 20° for 3 weeks + 9° for 8 w. flower earliest and simultaneously in spring; that just as before, those of 11 w. 9° flowered very irregularly, but those exposed first to 20° for 3 w. and then to 9° were quite uniform.

So that was the most suitable summer-treatment for Darwin-tulips, that were to be forced. And this is reasonable. For in 20° (and 17°) the flower-formation progresses most rapidly and the flowers show less irregularities than in 9°.

Let us now further consider this summer-treatment: 3 w. 20° and next 9°. After those 3 weeks 20° the flower had averagely reached stage III in 1924, i.e. the outward tepals are all visible as individual organs; the bulbs in 9° are still merely leaf-forming. (See N⁰. 19, Tab. 22.) If we had exposed to 20° for 5 w. and then to 9°, the flower-formation was quite finished on transition from 20° to 9°. (See also Tab. 22.) But already by that time the successive number of flowering in the field has become 4 instead of 1. Accordingly it is not at all necessary, nay undesirable, to wait for a celerrimal flowering (most rapid flowering) till all floral parts have been formed in 20°. Besides it is worth notice (see tab. 15 in N⁰ 19) that the joint number of floral parts, if we transfer after 3 w. or 5 w. from 20° C. to 9°, amounts resp. to 16.10 and 16.55, i.e. shows no difference (0.45) worth mentioning, whereas the flower is in stage III after 3 w. 20° in 1924, quite finished after 5 w. On regarding the mean errors of Tab. 16 and the fact (s. Tab. 15), that the chief difference between 3 w. and 5 w. 20° is still found in the tepals already for the greater part formed (0.35 in the tepals and 0.45 for the joint number), whereas more floral parts might be expected "earlier in 9°", the noticeable fact is observed, that when the flower is well-started in 20°, transition to 9° may take place. It is striking that 3 w. 20°; besides a rapid finishing of the foliage-leaves has such results, that the number of floral parts is brought to 16—16.5 instead of ± 21, when flower-formation is started and continued both in 9°. Even this increased number often produces transitional forms of the organs, frequently attended with the flower growing crookedly on the stalk.

So starting in 20° and an early transition to 9°, has been the base for the experiments on early-flowering, described in this first part. (For the sake of application this was already communicated in Laboratory-communication N⁰. 19, p. 7; = p. 1073 of these Proceedings, Vol. 34, 1925),

We shall see in this paper, that for succesful experimenting we are indeed compelled to mind the stage, in which the flower is, before the temperature is changed, and that it does not suffice to fix a certain date, as in the successive years this varies according to the climate to which the plant has been exposed in the field in the previous months.

What can be given in this first part on Early flowering of Darwin tulips is by no means complete. Though the results were an uncommonly early flowering for the Pride of Haarlem — yet I did not intend publishing until further modified experiments were made this year. But this division in at least two parts seemed better to me after all: 1⁰. the result as far as it could be ascertained hitherto, is sooner known to everybody who wants to apply or to experiment in this sphere; 2⁰. a description of the experiments of 2 or 3 years at a stretch would grow too long-winded for the readers; 3⁰. if for shortness' sake at the end of the experiments we give only the results of the exposures which ultimately lead to earliest flowering, we lose the whole connection with the preliminary experiments which indicated the direction how we could gradually attain that celerrimal flowering. Besides the proof-material is lacking which treatments are wholly unfavorable, which fairly favorable, e.g. in producing a somewhat later flowering. Besides various results of no value for practical purposes, may be of botanic-scientific importance. In such results economical interest is concentrated to those treatments having a celerrimal or optimal effect, but scientifically it is of at least as much importance to know the extreme treatments, the limits, either high or low temperatures, at which the flower-formation becomes impossible or shows abnormalities.

§ 2. *The beginning of the experiments and the influence of one and the same temperature.*

We received the lifted bulbs (from VAN TUBERGEN of Haarlem) already early in 1925, but the internal condition round the growing-point accorded fairly well with what we found in the bulbs of Pride of Haarlem a few weeks later in previous years. I.e. the temperature-exposures were started in 1922 on July 20, number of new foliage-leaflets in formation 2 or 3 — in 1924 on July 15 number of foliage-leaflets in formation 1 or 2, i.e. about 1 less — in 1925 already 2 foliage-leaflets had been formed on July 3. *From this it appears that the more or less advanced interior state of the bulb must be ascertained and we cannot rely on the date.* In 1925 namely the state of the growing-point on July 3 was intermediate between July 15, 1924 and July 20, 1922, whilst in those years the main bulbs were sent to us as soon as possible after lifting and had not been kept in a high temperature at the grower's.

The bulbs were kept in 20° from July 3—July 31, i.e. 4 weeks, then put in 9° for a long time. Besides on July 31 10 bulbs were fixed in alcohol 96 % and examined *later.*

It appeared *later on,* that in that transition from a short time 20° to a long time 9° the length of the outer young foliage-leaf in the bulb (which is to appear from the bulb later with the other leaflets as "nose" (tip)), was as a rule 3.0 to 3.5 mms. long. For the rest the flower was already in stage VI to VII. This appeared later on, and on comparison with other years (see above) we could safely (according to the field-cultures) have put the bulbs in 9° a little earlier, i.e. when stage III has been attained (outer whorl of tepals split off as 3 *individual* organs). This will be taken into account in the new series of experiments of this year. Doing so is also of practical importance; but if this sure method is thought to take up too much time or to be too difficult, the transition from 20° to 9° may fairly safely take place 3 or 4 weeks after lifting.

These bulbs were planted for early flowering on Sept. 7, 1925, in groups of 8 in boxes measuring 25 × 40 cms. and 21 cms. deep. (This year we are going to use groups of 6 in much smaller boxes). On Sept. 7, so on planting, the length of the outer leaflet, i.e. of the "nose", varied from 17—20 mms. in 9 bulbs. It seems to me, as far as we know at present, certainly not advisable to plant later. But fixing the date of *transferring* the bulbs from 20° to 9° (see above) requires much greater precision. For by that time they are in the midst of the rapidly progressing flower-forming period; — if the planting occurs at the beginning of September a week earlier or later *may* have its influence, but the organs of foliage-leaves and flowers are simply more or less long ; by planting somewhat earlier or later the chance of producing an injurious effect is by no means so great and the temperature remains the same (9°). Yet it is important for studies on earliest flowering to consider if that flowering may be accelerated by *planting* more or fewer weeks after the *transmission* from 20° to 9°.

The Darwin tulips thus treated were all planted on Sept. 7, 1925, viz. groups of 8 in 16 boxes. Besides the division in the actual experiments was started by that time. For the theoretical study of most rapid stretching the 1st was placed in 17°, the 2nd in 12°, the 3rd in 9° and the 4th in 5° C. — moreover 6 boxes were placed in 9° and 6 in 5° C. These 'stores' in 9° and 5°, served for experiments to be further described, in which after a shorter or longer period, i.e. with a shorter or longer "nose" length (= the outer leaf growing from the bulb), the boxes were transferred to higher temperatures (see § 3). We shall first describe how the stalks with leaves mainly behave, if they remain from the planting on Sept. 7 in 5°—9°—12° à 13° and 17°. From this it may be concluded whether *change* of *temperature* is *necessary* to attain the earliest flowering and cannot be substituted by continuous application of one certain average temperature.

The first shooting of the roots.

After about 4 weeks i.e. at the beginning of Oct. we noticed that the bulbs in 5°, 9° and 12° lifted up the soil, i.e. it appeared that the shooting roots did not go down well, but lifted up the bulb and some cms. of soil on top of it. This had to be redressed directly; all the bulbs were carefully replanted in looser sandy soil and the rest of the empty hard *outer brown scale* was removed. This namely greatly impedes the downward growth of the roots. For early flowering it is advisable as, I think, some growers also do — to carefully remove that outer scale *on planting*. Besides we could now observe the effect of the temperature on the shooting of the roots after 4 weeks. In 17° not a single root had shooted ; in 12° all the bulbs had roots the longest of which were already 4—7 cms. ; in 9° the shooting of the roots is most advanced, the longest is already 6—10 cms. ; in 5° the longest roots are 4—5 cms.

Accordingly 9° already shows a "celerrimum" in the shooting of the roots (most rapid ; we might call it an optimum, but who knows whether this is really most favorable, whereas we do know it is most rapid, so a celerrimum).

Besides 12° and 5° are also well-advanced, 12° slightly more so than 5°, while 17° is lagging behind. We shall revert to this subject, so remarkable with a view to the revision of the current botanical conceptions of optima, in connection with the other organs.

Only when the foliage-leaves ("the noses") had grown 9 cms .or more from the bulb, they were put in the light in constant hothouses. *In the bulb itself* we find by that time 4 cms. of the stalk with leaves. As throughout 5°

remained far behind other temperatures, they were not continued in 5° in the light, because this experiment would have been too expensive, but they were transferred to 13° (light).

The results of continuous 5°—9°—13°—17° from Sept. 7 follows in the table subjoined.

Length from the tip of the bulb to the apex of the leaf in mms.

Length from the tip of the bulb to the apex of the leaf in mms.

	5°	9°	12°/13°	17°
Nov. 10 '25	16.7 mms.	30.3 mms.	25.5 mms.	20.9 mms.
Nov. 24	26.5	60.5	41.1	30.8
Dec. 1	38.6	91.6	54	38.4
Dec. 8	53.7	157.0 L	68.6	44.5
Dec. 15	81.1	188	100.3 L	50.6
Dec. 22	90.5 L.13°	216	130	59
Dec. 29	↓ 152	266	189	66.5
Jan. 5 '26	276	327	257	85 — L Jan. 12
Jan. 27	411	403 (310)	373 (444)	149
Febr. 9	428	435 (340)	386 (531) *	190
March 10		444 (358)		210 (450) *

The data of Tab. I up to and including Jan. 27 are also graphically represented in Fig. I. The temperatures are plotted on the abscis. Those of 12° C. have got to 13° C. on transmission to light for technical reasons. The temperatures give the degrees of heat of the soil in the boxes, as long as the largest growing part is still found there. When leaves and stalk have grown some way and the boxes are moved into the light, the temperature among the plants above ground is constantly kept at 9°, 13°, 17°, because by that time (at least with the tulip) the most important part of the stretching takes place in the air. On the day that the boxes are put in light, an *L* is placed in the table behind the linear measure. On the ordinate (Fig. 1) the linear measure is placed to the left; to the extreme right the date of observation. In the table the figure between brackets from Jan. 27 denotes the distance from the tip of the bulb to the lower side of the flower, i.e. the length of the stalk to which is added ± 40 mms. inside the bulb. The period of full bloom has been indicated in the table with an *. In small print the length of the plants outside the bulb has been given, after transmission from 5° to 13°.

Lengte in cM. = Length in cms. Datum = Date.

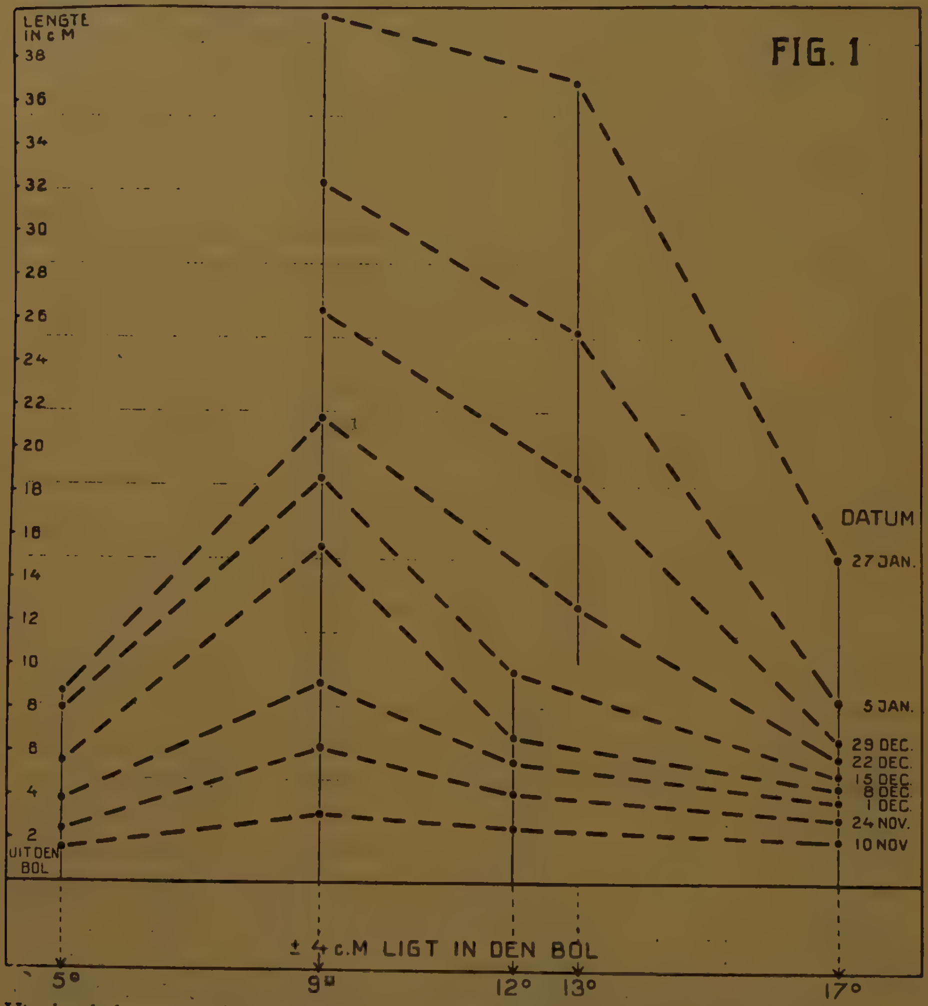
FIG. 1

Uit den bol = out of the bulb. cm. ligt in den bol = cms. are in the bulb.
For explanation the text should be consulted.

From table and figure the following conclusions may be drawn. (The figures always represent an average of 8 bulbs.)

1°. The stretching of the main-axis with leaves, e.g. from Nov. 10 to Dec. 22 yields exactly the same picture as we have observed in the shooting of the roots: *in 9° most rapidly,* in 12° distinctly less rapid than in 9°, in 5° less rapid than in 12°, *in 17° slowest.*

2⁰. Those in 12° and later (in light) in 13°, were the first to flower of these groups (Febr. 9); those in 5°, were continued in light in 13° (small printed figures in the table) and flowered some days later than those constantly kept in 12°—13° C. Those of continuously 17° flowered as late as March 10. But in the temperature, which causes "most rapid" progress for months together, i.e. 9°, the flowers remain in bud, green, even up to ± March 15; while both light and moisture of soil and air are perfectly identical to those in 13°.

3⁰. Accordingly none of these temperatures, *continuously* applied, is conductive to *early* flowering. And 9° is the only suitable temperature for months at a stretch. When the Darwin tulip has reached stages III to V (the progress is very quick then) in 20°, i.e. about 3 or 4 weeks after lifting, the bulbs remain from Aug. 1 to e.g. some days in Nov. in 9° to promote celerrimal stretching (and have meanwhile also been planted into boxes ± Sept. 1).

4⁰. Starting with 20° followed by one temperature, e.g. 9° for months together will not do for a celerrimum, but we must find out at what time of growth we had better transfer from a low temperature to another. This is also known to the growers, but we must try to approximate and fix this point of time in the growth as exactly as possible.

This will be discussed in the next §.

But it should be borne in mind that this is a first part and a new series of experiments follows made in 1926.

§ 3. *By what change of temperature may the earliest flowering be attained?*

Simultaneously with the experiments described above in constant 5°—9°—13°—17° some (6) boxes (planted on Sept.) were left in 9° and 6 transferred form 9° to 5°.

From these two boxes were taken from 5° and two from 9° and one of each placed into 17° and into 20°, when the length of the "nose", i.e. the distance from the tip of the bulb to the apex of the leaf (in which measure extention of stalk and leaf are mingled) amounted to *averagely 3 cms.* Next again 4 boxes were transferred, one from 5° and one from 9°, respectively to 17° and 20° when this measure amounted to ± *6 cms.* On reaching a length of 9 cms. (or longer) all were put in the light and besides those from 20° somewhat cooler, viz. in 17°. Those still kept in the dark in 5° and 9°, protruding ± 9 cms. from the bulb, were directly moved into 17° light and by way of control one box from 5° and 9° to 23°. They remained there for a short time till the flower-bud became visible, when they were also transferred to 17°.

In order to get a survey of this set of experiments, this is repeated in the following schematic representation:

After lifting all 20° for 4 weeks, next all 9°, on Sept. 7 planted into boxes (each containing 8 bulbs). One box was constantly kept in 5°, one in 12°—13°, one in 17°, as has been described in the preceding §. Moreover on Sept. 7 6 boxes were planted in 5° and 6 in 9°.

These were treated as follows:

Mode of treatment. Length of the plant out of the bulb.

	Upwards of 3 cms.	Upwards of 6 cms.	> 9 cms. light.	Flower-bud visible.
9°	→ 17°			→
9°	→ 20°		→ 17°	→
9°		→ 17°		→
9°		→ 20°	→ 17°	→
9°			→ 17°	→
9°			→ 23°	→ 17° →
5°	→ 17°			→
5°	→ 20°		→ 17°	→
5°		→ 17°		→
5°		→ 20°	→ 17°	→
5°			→ 17°	→
5°			→ 23°	→ 17° →

The results of these experiments are summarised below from figures 2—6, giving a graphical representation of them, also from § 2, from Nov. 10.

For comparison with figs. 3—6 fig. 2 repeats the results of constant 5° (in light 13°, then dotted line), constant 9°, 13° and 17°. The figures are found in Tab. I, so they are not repeated here, the graphical representation is connected with figs. 3—6, consequently differing from Fig. 1. Here the data of observation are placed along the basal line at proportional distances of time and the length of the part grown from the bulb erected vertically upon it, indicated by a dot. The temperature has been given at the line of growth, and on transferring to another temperature, the new temperature has been recorded behind that date, behind that dot. A transfer to light is indicated by a cross-stroke with an *L* above it. The date on which the group concerned was in full flowers, has been indicated by a rosette with a central dot.

A. H. BLAAUW: “RAPID FLOWERING OF DARWIN-TULIPS”. I.

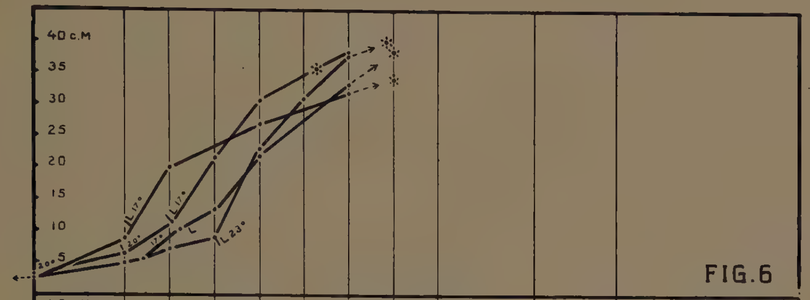

FIG. 6

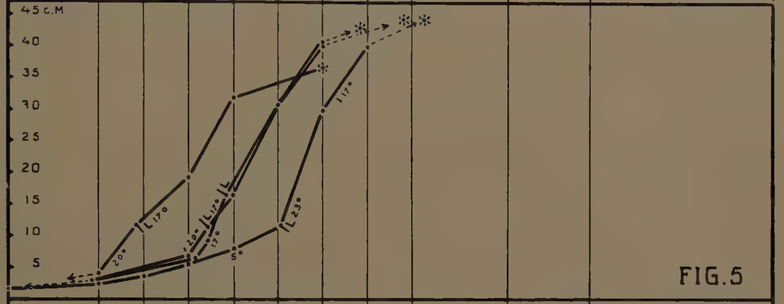

FIG. 5

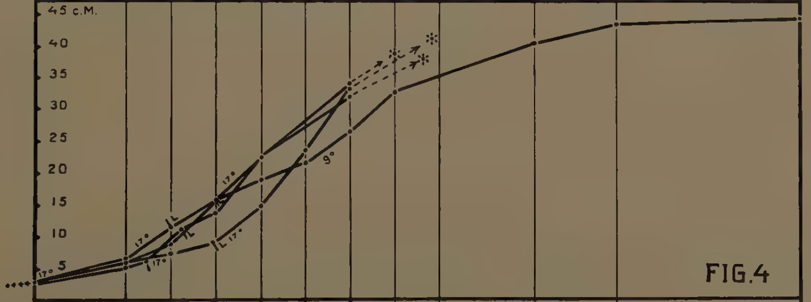

FIG. 4

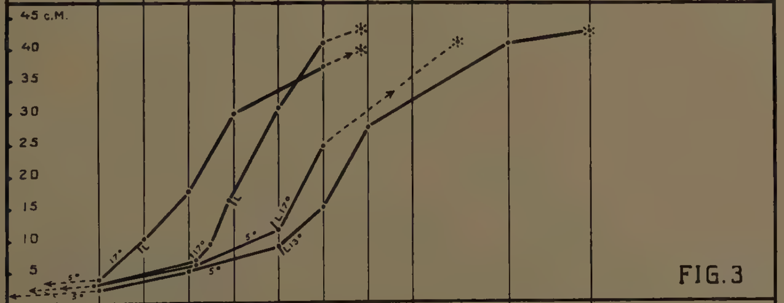

FIG. 3

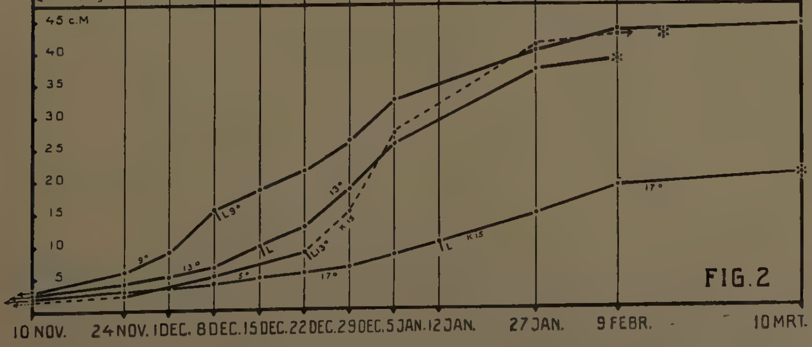

FIG. 2

Fig. 3 gives four lines of growth, viz. it first repeats a curve of fig 2, concerning some 8 tulips stored in 5° and transferred to light in 13° on Dec. 22 (length from the bulb 90.5). Besides three curves, when from 5° (since Sept. 7) the bulbs are transferred to 17° C. at a "nose"-length of upwards of 3 cms. — upwards of 6 cms. — and upwards of 9 cms.

1^0. On conveying from 5° to 17° we directly notice a considerable acceleration of growth. An increasing acceleration of growth and earlier flowering compared to 5° and afterwards 13°.

2^0. The strongest acceleration of growth we find on transferring from 5°, upwards of 6 cms. to 17°. Then this group equals in growth and bloom the one put in 17° already at 3 a 4 cms. The full flowering occurs on the same days (Jan. 4). The third group transferred to 17° does not flower until Jan. 19.

3^0. Whereas we saw in Tab. I and Fig. 1, that on Dec. 8, 15 and 22 a constant exposure to 17° was unfavorable compared to 5°, we see the striking fact, that when the bulbs have *first* been exposed to a *lower* temperature (here 5°) and *next* 17°, a much more vigorous growth and earlier bloom is attained than when the low temperature is still continued. *Accordingly about that time the celerrimum of growth and flowering is shifted from a lower to a much higher temperature.*

We shall not add any separate tables of figures from which all lines of growth have been composed. Every one can read and measure these lengths and data from the figures.

Fig. 4 repeats "constant 9°", even on March 10 still closed as green flower-buds. The difference with 17° is not so striking now as in fig. 2, also because "constant 9°" were first rather vigorous growers, but yet it is evident that earlier or later transmission to 17° after some time causes more rapid growth than 9°, while in previous months 9° most of all others excelled 17° far in rate of growth (see fig. 1). Here too the celerrimal temperature of 9° is moved upwards at a certain point of time, i.e. with a certain length of the plant. All three groups transferred from 9° to 17° attain full bloom from Jan. 5—12; the earliest (Januari 5) those which were moved to 17° at upwards of 6 cms.

Now let us compare fig. 5 with fig. 3. In fig. 5 we do not transfer to 17° but to 20° from 5°, at an average length of upwards of 3 cms. and 6 cms, besides 8 tulips with a length of nearly 12 cms. were transferred from 5° to 23° C. The curve of fig. 3, where we transferred from 5° to 17° at a length of upwards of 6 cms., was repeated, as giving the quickest result in those experiments of fig. 3.

What may be concluded from this? 1^0. That the first transmission from 5° to 20° (and a short time after in light to 17°) gave the most rapid flowering (Dec. 29); 2^0. that when at a "nose"-length upwards of 6 cms. the bulbs were put in 20° for some days, the progress of growth is fairly identical to the growth of the bulbs directly put in 17°; — the flowering of the group 15° — 6 cms. 17° was a week earlier (Jan. 4) than of 5° — at 6 cms. 20° (for 3 days, next light 17°). We must not attach too much value to this difference, because 5° — 6 cms. — 17° was not put in light until a length of upwards of 16 cms. had been reached and 5° — 6 cms. — 20° already at a length of 11.5 cms. We are now investigating whether light or dark in these days plays an important part; this will be discussed in the 2nd part on early Flowering. 3^0. transferring from 5° to 23° when a length of 12 cms. was attained gave us a hint. For though this group was kept a long time (up to Dec. 22) in 5°, before that length had been attained, 23° (in light) gives a considerable acceleration of growth; only when the bud shows from the leaves, they are transferred to 17° and are in full flowers on Jan. 14. The stretching however is so forcedly rapid, that the insertion-spot of the upper leaves along the stalk often grows together with the stalk and causes the upper leaves or outer tepals to be torn. This method is not recommended, though it proves, how accelerating an influence a high temperature can have in *that later period*. It might be expressed in this way, that here for a short period of time the celerrimum (most rapid) is found in a higher temperature than the optimum (most favorable).

Finally Fig. 6 gives the most important result. On transferring after that initially celerrimal temperature of 9° to 20° at ± 3 cms. or upwards of 6 cms., it appears that "transferring to 20° at 6 cms." gives *the earliest flowering* of all experiments hitherto made, viz. on Dec. 24. Indeed those transferred to 20°already at 3 cms. first exceed a good deal in growth, but they are overtaken by those moved to 20° a fortnight later (± 6.8 cms.), as to growth in length and early flowering. And though they remain *in 20° but one week* before being removed to 17° in light, they do flower 10—12 days earlier, than the group directly put in 17° at 6 cms.

A photo of the first red Darwin-tulips flowering at Christmas, is shown in fig. 7 (Plate).

In various ways the experiments are continued on this base. That base consists in this, that the Tulips, 3 or 4 weeks after lifting, preferably controlled, viz. till at least the outer tepals have been formed, are kept in 20° next in 9°, after 4½ to 6 weeks planted in boxes in 9°, and only then, when the plant has grown from the bulb ± 6 cms., are transferred to a higher temperature (preferably 20°).

The above is however repeated and varied to discover whether e.g. that temperature should be more or less raised or lowered; whether at 6 cms. an exposure to dark up to ± 10 cms. (as we did now) is really better than directly to light at 6 cms. etc. These subjects will be treated in the 2nd part on Early Flowering of Darwin-tulips and later likewise in a paper on Early Flowering of Early Tulips.

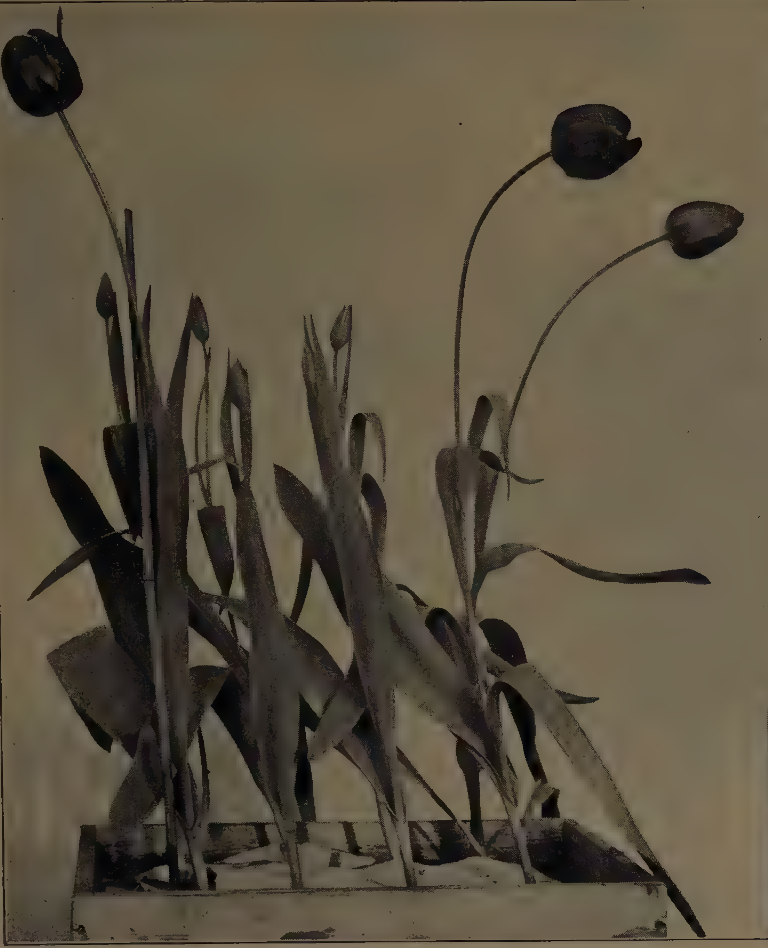

Fig. 7. Pride of Haarlem, flowering on Christmas in Holland; — $3^1/_2$ week in 20° — afterwards 9° until 6 cm. above the bulb (Nov. 24th) — then 20° at first dark and in light 17° (see the text).

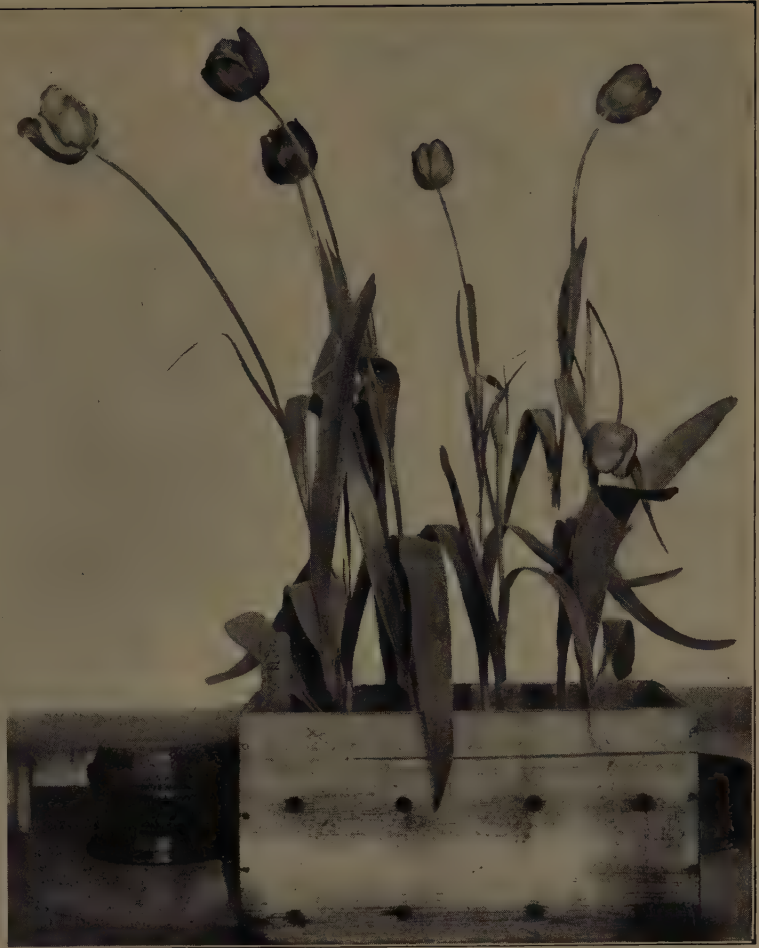

Fig. 8. Flowering in the first week of January, with example of a withering Flowerstalk (the right one).

§ 4. *Conclusion first part.*

So it is possible to get the Darwin-tulips Pride of Haarlem flowering at Christmas without abnormally early lifting or particular technical means. In the above it has been sufficiently described (summarily), how from 65 temperature-combinations between lifting and planting one most rapid and favorable mode was chosen (9° was most rapid, but not best) and how this summer-treatment served as a base for treating in 16 various modes after the planting in boxes to the flowering. That of those 16 there was one exceptional group flowering at Christmas and some other groups flowering 5—10 days later.

In the second part this celerrimal flowering will be repeated and different slight variations will be made to investigate whether the results are corroborated and may possibly be somewhat accelerated or improved.

Now we have still to point out a reverse in our experiments. Two "mistakes" appeared in the various groups, so that only half the number of the plants got to full bloom. Firstly in part of them the extension lags behind the others at a certain point of time and the flower-bud with the top-part of the stalk gets a withered strawlike appearance. This is not due to forcing, it occurred in the lower temperatures as well as in the higher. Nor can it be possibly owing to a dry atmosphere, for it occured in a degree at least equally strong in very moist air in small glass boxes (e.g. thermostats of 13°). Secondly we also observed in our experiments the phenomena of the tipping flowerstalks. Just as the withered flower-buds, it occurred in low temperatures as frequently as with the tulips transferred to a high temperature, also in very moist rooms.

Fig. 8 (Plate) represents a group on Jan.13 (transferred from 9° at 9 cms. length to 17°). It shows the Tulip to the extreme right in full bloom completely broken. The different hue of the rest of the Tulips is but seeming, as two are in the shade, others in sunlight. We also notice a short stalk with "straw-like" flower-bud between the leaves. The tipping occurred in our experiments, when the flowers were still in bud, but as well when the flower was in full bloom or even when it was beginning to fade. The spot where the stalk snapped lay as a rule 8—12 cms. below the flower. For further description of this phenomenon VAN SLOGTEREN's papers and further investigation should be consulted; and further STEVENS a. PLIMKETT "Tulip Blossom Blight" Bull. N^{0}. 265, Agr. Exper. Station, Univ. of Illinois.

Certainly it is not due to forcing in higher temperature, and therefore we mention, that it did not occur in the box flowering at Christmas. This did yield however four flower-buds that remained strawy. But as already stated this likewise occurred in constant 13°, etc. For the rest we shall not go into these phenomena any further; we shall only record in the second part whether this year in somewhat altered treatments the two phenomena re-appear in an equally strong degree.

Besides we wish to mention here that a box, come to bloom with some broken flowers and a few withered buds was emptied. It appeared that the soil was sufficient and moderately moist and the root-system looked equally healthy in all of them.

Besides on the description of the experiments and the way in which we attained this flowering so early for Darwin-tulips, I mainly emphasized those parts essential for practical purposes. Meanwhile in the data of this and of previous papers there are found many things interesting from a scientific-physiological viewpoint and requiring profounder investigation. All this may be found in the preceding; but I wish to emphasize some cardinal points, because they make us ask about the inner causes of these phenomena.

1°. We know now that the formation of the last leaflets and of the floral parts progresses most rapidly in 20° C. (also fairly rapidly in 17°), in the first 3 or 4 weeks after lifting. This concerns the organs formation; that celerrimum is comparatively low, considering the "optimal" temperatures found for other processes, as respiration and assimilation. But in our researches we have to deal with *the plant as a whole.*

2°. Even more astonishing it is to the botanist used to those high "optima" of simpler physiologic-chemical processes, that the plant, studied *as a whole,* shows us — when the first floral parts have been formed — a very low celerrimum of 9°. That which according to the standing phrase is called the optimum, is shifted rapidly downwards, when the first floral parts have been formed and is found at ± 9° C. And this for months at a stretch. A higher temperature, as 13°, gives a slower development, 17° still slower. In that 9° C. the flower is finished, the stalk, the young foliage-leaflets, the floral parts increase in size most rapidly in that temperature. What is the cause of this, that the celerrimum falls so strongly and continues so for months together? Because from the process of *organ-formation* we proceed to the process of organ-*enlargement?* But even then a celerrimum ("optimum") of 9° is particularly low.

3°. After ± 3 months, when the length of the plant (the part still inside the bulb, plus length of the leaves growing from the bulb) is 8—10 cms. — the optimum of growth is shifted to a higher temperature and we are obliged to transfer to ± 20° for a celerrimal stretching and flowering. This fact is almost more surprising. Whereas for so many months, for what we might call the "little stretching" the celerrimum is found in ± 9°, at a certain length, which requires rather great precision, the celerrimum is moved rapidly upwards to ± 20°. Where it will be exactly found, we shall further investigate in the second part. But to what is it due, that the "little stretching" with a celerrimum of 9° for months together passes into the "great stretching" progressing most rapidly at ± 20°? If in Aug. the bulbs had been left and planted in 20° or 17°, everything would have progressed very slowly and the flowering would have occurred in March. If after 20° they had remained in 9°, the result had even been worse (see above "constant 9°"). It is exactly 9° for months together followed by ± 20°, which yields flowers as early as the end of Dec.

Such instances of exposure to cold then finally to heat with a view to early flowering are familiar to practice. To determine these temperatures and periods more exactly is the first task of these researches. But here botanical science is put before questions with which it has been too rarely occupied and which teach us, that *from a botanical point of view we have first of all to mind the behaviour of the plant as a whole,* before entering upon the deeper and more detailed processes of finding an explanation for that behavior. With this botany and application will both be served.

August 1926.

Geology. — *"On Fossil Cetacea and Pinnipedia in the Netherlands."*. By A. B. VAN DEINSE. (Communicated by Prof. MAX WEBER.)

(Communicated at the meeting of October 30, 1926).

In "De Bodem van Nederland" (1855—1860) by W. C. H. STARING it says on p. 216, that as early as 1837, so well-nigh a century ago, molars and vertebrae of *Squalodon grateloupi,* Herman von Meyer were found in the environs of Eibergen. On the following pages 217—219 STARING enlarges upon findings of fossil Cetacea in our country, and on p. 209 we find some additional data concerning them. On p. 219 he concludes by saying: "We have dwelt for some length on this Squalodon in order to emphasize the great significance of finding and preserving even a few bones or fragments of bones for our knowledge of primeval animals. A comparative study of some bones enabled us so to speak to reconstruct to all appearance the whole animal. It is desirable, therefore that similar finds should by all means be made accessible to science and not be left dispersed in possession of private persons, or be kept isolated in sundry remote places, where no books or collections are available for an indispensable comparative examination."

Thus STARING wrote already 70 years ago. What has been done in this field since that time? The very opposite of what he suggested. Numberless persons and corporations in Twente, Achterhoek, and Westphalia have been making collections during many decades without any guiding principle, or without any cognizance of the work of other observers in the same domain. The exact localities have been vaguely indicated, or are altogether unknown. Rare fragments have been carelessly shifted to other places or have got lost; only a few of the hundreds of unearthed fragments have been saved from oblivion in our State-Universities, in Museum Teyler, or in collections of Educational Institutions. Hardly any have been properly determined.

True, some collectors have endeavoured, with partial success, to save some beautiful fragments: amongst them R. E. DE HAAN, 1882, the learned Director of the H. B. School at Winterswijk, who in his "Beknopt Leerboek der Delfstof- en Aardkunde" also treats this subject on pp. 45 and 212, and who corresponded with Prof. HUBRECHT on teeth of Squalodon (now Scaldicetus grandis, du Bus). A letter from DE HAAN to HUBRECHT is still preserved together with a tooth of Scaldicetus at Utrecht in the Zoological Museum and Laboratory.

Furthermore WICHMAN, LORIÉ, P. TESCH, DUBOIS, MAX WEBER, and a few others have collected material, but have not or only partly denominated it. Since after STARING, next to nothing has appeared in our country on this subject, STARING's "Bodem" was still the standard work relied on, so that even now the majority of the fossil remains of Cetacea in our country are given the name of Squalodon, or have no name at all. I have seen numerous fragments with the invariable inscription "Squalodon", while nobody knew what could really be classed as such and what not.

What adds to the chaos is that the name "Zeuglodon" is occasionally met with (De Haan Beknopt Leerboek, vide supra p. 212 and STARING's "Bodem", p. 216). In the Geol. Mineral Collection of the Utrecht University a fragment of a skull of a fossil cetacean was called "Zeuglodon verdense" derived from Zwilbroek near Groenlo, while on the skull a label was stuck with the name "Squalodon Grateloupi (?) v. Meyer", miocene 1887. In August 1925 I found in the Museum for Natural History of Brussels that this skull-fragment, much injured alas, originates probably from Eurhinodelphis Cocheteuxi du Bus, Upper Miocene. So far as we know now, Zeuglodon occurs in Europe only in England, to wit Zeugl. Wanklyni Seeley (1). Some relation was also often suspected between the Pinnipedia and the fossil Cetacea (STARING pp. 217, 218). This looks the more ominous, as genuine specimens of this group really occur in our country as fossils in the same localities where fossil cetacea are found. We shall discuss this later on.

Of the copious material of fossil Cetacea from our country only three fragments have been properly described and pictured. Plate III in STARING's "De Bodem" shows us a caninus of Squalodon Grateloupi H. v. Meyer, now called Scaldicetus grandis du Bus in the new nomenclature of Abel. On the same plate we see a molar, according to STARING also from Squalodon Grateloupi H. v. Meyer, now after Abel (5) from Squalodon Antwerpiensis P. J. van Beneden. Both pictures are excellent. The two fragments are now in the Geol. Museum of the Leyden-University. Not until 1917 did M. WEBER (2) give a description and a picture of the third, and up to this day the last specimen of the native fossil Cetacea, viz. the skull of Choneziphius planirostris G. Cuv. found in the West-Schelde and preserved in the above-named Leyden-Museum.

In VAN BAREN's new edition of "De Bodem van Nederland" (3) we read on p. 386 something about the Miocene of the Netherlands and about the fossil Cetacea found there. Already in 1778 J. A. DE LUC found among other things dorsal vertebrae of whales, which were recognized by P. CAMPER. They were found below Delden near Twikkel; these findings have also been mentioned by STARING (4). I suppose some of these vertebrae are still present in Teyler's Museum. Others, which found their way in the Museum of the Groningen-University with Camper were destroyed in a fire in August 1906. VAN BAREN also makes mention (p. 386) of the genera Squalodon and Scaldicetus; he does not mention other genera.

For some years we know already from WEBER, TESCH and others that not all that has been referred to the genus Squalodon can be classed as such; the said investigators have warned me before against this. In August 1924 I started my examination from Enschedé with unexpected succes. Through Miss P. S. L. v. DEINSE and Mr J. J. v. DEINSE I made the acquaintance of Mr M. J. v. SAMBEEK, Lonneker near Enschedé, who on my very first visit kindly lent me a humerus of a fossil cetacean, while we found on the same day a mass of material at Hengelo at the houses of Mr SCHIEDAM, VAN HOUTEN, LANGERHUIZEN and SCHOENMAKER. Part of a trunk, two humeri, an enormous cavitas glenoidea of a scapula, many vertebrae were shown me and kindly given me as a loan.

At Enschedé two very large and fine collections of Messrs VINKENBORG and REGELINK came under my notice through the kind assistance of Mr VAN SAMBEEK, who also granted me free access to the collection of the "Enschedesche Museumvereeniging". Moreover Mr J. J. VAN DEINSE stood me in good stead as President of the Archaeological Society "Twente" where also much material is present. Afterwards I still got acquainted with the collections of the TEN BOKKEL HUININK family of Nede, Mr JANSEN and Mr STEGEMAN both of Winterswijk, while also Mr. TEN HOUTEN of Winterswijk and Messrs LANDMAN and VAN BEMMEL both of Winterswijk rendered me great service. Finally I received material from Messrs J. G. C. DE GROOT of Eibergen, from J. W. TE WINKEL of Miste near Winterswijk and from Mr J. WAGNER of Ellewick near Vreden in Westphalia. Truly, material, data and assistance enough and to spare!

In October 1924 I was examining part of this material in the Museum for Nat. Hist. at Brussels with Prof. L. DOLLO Sc D., who assisted me wherever he could. Also the skilled preparator H. MENSCHAERT, who spent a lifetime at the Museum, was of great help to me. I feel greatly indebted to all those for their most useful assistance in my work.

At Brussels I found that many fossil species of Cetacea occur in our country, besides the three familiar to us. With much more material, about 200 numbers, weighing ± 150 k.g. I was at Brussels again in 1925. In July 1926 I was able to study in Brussels another lot of bones together 40 fragments.

A small percentage of the fossil remains, not 10 %, could not possibly be found on account of a considerable amount of wear and the total absence of typical processes, articular surfaces etc. The species that were established, have been included in the subjoined list, every fragment coincided well with the corresponding pieces at Brussels. Besides the material lent to me by many collectors I myself have collected fossil remains in Aug. 1924 and 1925 in the Needschen Berg north of Nede, Gelderland, and in the famous quarry of Wiegerink, near Zwolle, not far from Groenlo, municipality of Eibergen. The latter locality is sometimes called "de Koerboom", anyhow by the Enschedé collectors. This may create confusion with "the Koerboom" meant by Staring and mentioned by him also on pp. 218 and 219. We have to do here with two different places, which in common parlance got the same name. "De Koerboom" of STARING was a brick-kiln (p. 218) that ceased to exist long, long ago, and was situated to the north of the road from Groenlo to the German border, about halfway. The loam-pits are fallen into disuse there. On STARING'S geological map it is made mention of and in two places the Upper-Miocene is indicated as "tertiary loam of Eibergen". Those grounds are part of the municipality of Eibergen. Now the quarry of Wiegerink, i.e. the new "Koerboom" lies to the south of the said road and has large loam-pits, partly in disuse, partly still in exploitation. By this new "Koerboom" is meant the stone quarry "de Hoop" (STARING p. 218), now the property of the firm FERNIER, OVERKAMP and WIEGERINK, formerly WIEGERINK BROTHERS. Here also the loam is Upper-Miocene. On STARING's Geological Map the Wiegerink quarry is located due north of the quarter of Zwolle. The loam of both places is of the same formation and there is sure to be some similarity in the underground of all this grey loam. Nowadays fossil remains of Cetacea and Pinnipedia occur only in the Wiegerink-quarry.

Is is extremely regrettable that all the material handled by me, belongs to so many persons. After all had been studied it had to be distributed again and was broken up for ever. I was allowed to keep only a few fragments. Of the material that had to be returned I had good photo's taken, or I had plaster-casts made if the fragments were rare or very beautiful. I made 14 casts myself after DR. W. F. J. MILATZ of Rotterdam had taught me that art. About 60 fragments have been preserved in 180 photos taken from various sides. Future material will be treated as the above, for which I have received many promises of collaboration. In a later paper I hope to revert to this subject in detail. It goes without saying that in spite of my assiduous searching in Twente and Achterhoek, many pieces must have escaped my notice, but this will now occur less frequently with the present systematic collaboration.

The fossil Cetacea from Achterhoek are of the same antiquity as the great abundance of remains, found between 1860 and 1863 during the building of the fortifications round Antwerp (6), (7), the greater part of which is now at Brussels. In the interjacent grounds near Reek, in the neighbourhood of Grave on the Meuse, boring 41 of the "Rijks Opsporing van Delfstoffen", a crown of a canine of Scaldicetus grandis du Bus has been discovered which is now preserved at Harlem in the collection of the "Rijks Geologische Dienst". In November 1924 Dr. P. TESCH was so kind as to draw my attention to this find. This crown agrees entirely with the one, pictured by Staring in "De Bodem" on plate III (vide supra). From the following list of recognized fossil Cetacea and Pinnipedia in our country it appears that, truth to tell, we do not possess an ossuarium such as Belgium possesses in the environs of Antwerp, but that we have quite a good number of species and very much valuable material.

As said above, up to now only three genera were determined in Holland, every one with I species (Squalodon Antwerpiensis, Scaldicetus grandis and Choneziphius planirostris) (2, 3).

PROF. RUTTEN still obliged me by sending me for inspection a very good canine of Scaldicetus grandis du Bus, "found between Groenlo and Eibergen" by Dr. J. Lorié, the property of the Geol. Mineral Institute of Utrecht. Some fragments are still at Leyden. Beyond the above-named fragments of Squalodon and Scaldicetus, the molar and the canine pictured and treated by STARING nothing (so far as we are aware) exists in our country of these two genera. Neither is anything known of vertebrae up to now. It is remarkable, though, that for 70 years such a great amount of material from our country has been referred to "Squalodon", and that we know only now, that what STARING indicated as such, are still the only fragments to which the term can be applied..

It is just the same with Choneziphius. Besides the skull, treated by WEBER nothing is known of the other parts of this animal in our country. The three known genera and species just mentioned, are not included in the list. The odontoceti and mystacoceti have been recorded separately, while the list closes with a few fossil Pinnipedia, which are by far the least known in our country.

† ODONTOCETI.

Name:	Locality	Remains found
1. Acrodelphis macrospondylus Abel,	Wiegerink quarry.	8 caudal vertebrae, 4 lumbal vertebrae, 1 dorsal vertebra, 2 humeri.
2. Acrodelphis scheynensis Du Bus.	" "	1 caudal vertebra, 10 lumbal vertebrae, 2 dorsal vertebrae, 2 epistropheus, 1 humerus, 1 right radius,
	Dieters (?)	1 caudal vertebra,
3. Acrodelphis denticulatus Probst? or scheynensis Du Bus?	Meddeho near Winterswijk.	2 caudal vertebrae.
4. Acrodelphis sp.?	Wiegerink quarry.	1 epistropheus, 1 perioticum.
5. Cyrtodelphis sulcatus Gerv.?	" "	4 bullae, 4 periotica.
6. Cyrtodelphis sp.?	" "	1 bulla, 1 perioticum.
7. Eurhinodelphis Cocheteuxi Du Bus.	" " and Meddeho near Winterswijk.	1 lumbal vertebra. 1 humerus, 1 skull-fragment, 1 proc. zygomaticus of the right temporal-bone.

† ODONTOCETI *(Continuation).*

Name:	Locality:	Remains found:
8. Eurhinodelphis cristatus Du Bus	Wiegerink quarry Meddeho near Winterswijk and Miste.	5 caudal vertebrae, 2 lumbal vertebrae, fragment of the right maxillaire, intermaxillaire right and left; fragment of the right temporalis bone.
9. Eurhinodelphis longirostris Du Bus.	Quarry of Wiegerink and Miste near Winterswijk.	2 lumbal vertebrae. 2 caudal vertebrae.
10. Eurhinodelphis sp.?	Miste, Hooge Lutte near Oldenzaal, Wiegerink quarry	2 caudal vertebrae, 1 dorsal vertebra.
11. Thalassocetus sp.?	Wiegerink quarry.	3 teeth.
12. Unknown genera of Odontoceti?	„ „	2 teeth.

13. Ziphioids, not completely determinable, of which several caudal vertebrae and 1 dorsal vertebra were found in the Needsche Berg, Nede, Gelderland, at Meddeho near Winterswijk and in the quarry of WIEGERINK. A caudal vertebra, perfectly intact, from Nede, Upper Miocene, reminds us forcibly of a corresponding one of Ziphius cavirostris, which is recent. Among these Ziphioids no doubt some species occur. Furthermore some fragments of †Odontoceti could not be determined in detail. When adding Scaldicetus and Squalodon (vide supra) we have 13 species and about 7 genera.

† MYSTACOCETI.

Name:	Locality:	Remains found:
1. Amphicetus sp? van Beneden.	Wiegerink quarry, Nede.	2 lumbal vertebrae, 1 caudal vertebra,
2. Amphicetus verus? van Beneden.	„ „ „	2 caudal vertebrae, 1 lumbal vertebra.
3. Balaenoptera sp., van Beneden.	„ „ „	piece of lower jaw and pieces of skull-bone.
4. Balaenoptera borealina, v. Beneden. Bal. bor.? of musc.?	„ „ „	3 lumbal vertebrae, 1 dorsal v., 1st dorsal v. or the 7th cervical vertebra, 2 caudal vertebrae, 1 symphysis of the left lower jaw, 1 dorsal part of a costa.
5. Balaenoptera musculoides, van Beneden.	„ „ „	1 symphysis of the right lower jaw, 1 head humerus, 2 caudal vertebrae, 1 finger phalanx.

† MYSTACOCETI *(Continuation).*

Name:	Locality:	Remains found:
6. Balaenoptera rostratella van Beneden.	Wiegerink quarry, Nede.	5 pieces of costa, 1 dorsal vertebra, 1 caudal vertebra.
7. Balaenula balaenopsis, van Beneden.	„ „ „	6 lumbal vertebrae.
8. Burtinopsis minutus van Beneden.	„ „ „	3 dorsal vertebrae, 1 caudal vertebra.
9. Burtinopsis similis en Burt. Sp? van Beneden	„ „ „	2 caudal vertebrae.
10. Heterocetus affinis, v. Bened. en Heterocetus affinis?	Wiegerink quarry and Winterswijk (?). Meddeho.	9 dorsal vertebrae, 2 lumbal vertebrae, 1 caudal vertebra, 1 humerus, 1 petrosal bone, 2 bullae, 1 piece of the lower jaw right, costa?

The humerus of N⁰. 10 is a remarkably fine large specimen with a well preserved head. It is present in the Museum of Teyler's Genootschap, Harlem. It is the only one in our country. Prof. DUBOIS kindly informed me that the locality is probably the environs of Winterswijk. A plaster cast and three photo's were made. Brussels has similar specimens to this one.

11. Heterocetus brevifrons? van B. en Heterocetus sp?	Wiegerink quarry.	fragment of petrosal bone. Cervical vertebra.
12. Idiocetus laxatus, v. B.	„ „ and locality (?)	4 lumbal vertebrae.
13. Isocetus sp. v. B.	Wiegerink quarry.	1st 2nd and 3rd dorsal vertebra, 1 lumbal vert.
14. Mesocetus latifrons? van B.	Nede, Needsche Berg.	1st caudal vertebra, 1 dorsal vertebra.
15. Mesocetus longirostris van Ben.	Wiegerink quarry very propable, Nede. Miste near Winterswijk.	1 atlas, 2 epistropheus, cervical vertebra no. 3 and 4 or 5, 1 lumbal vertebra, 2 caudal vertebrae. Right ulna, proximal part; head of right humerus, piece of lower jaw, left; 3rd, 4th, 12th dorsal vertebra, 4th, 8th lumbal vertebra, 1st caudal vertebra, fragm. left temporal bone, 3 fragm. costa; piece of the right lower jaw near the symphysis, 1 finger phalanx, (eventually of Balaenoptera).

† MYSTACOCETI *(Continuation).*

Name:	Locality:	Remains found:
16. Mesocetus sp. van B.	Probably Wiegerink quarry.	1 lumbal vertebra
17. Plesiocetus brialmonti? van Ben.	Wiegerink quarry.	1 „ „
18. Plesiocetus dubius, van B.	„ „	1 „ „
19. Plesiocetus hupschii? van Beneden.	„ „	cervical vertebra 3 or 4, 1 cervical vertebra, the 1st dorsal vertebra.
20. Plesiocetus sp. van B.	Probably Wiegerink quarry.	1 caudal vertebra, 1 lumbal vertebra.

As appears from the above of the † Mystacoceti 9 genera and about 18 species were found. When adding to these numbers the † Odontoceti we get 16 genera and ± 30 species † Cetacea in our country. These figures must be considered provisional. The † Mystacoceti invariably bear the name of the author P. J. VAN BENEDEN and it can hardly be questioned that not all the names of species and genera can reasonably be maintained. Most likely some of them have to be combined, so that the number will diminish. In the Brussels Museum — where I made my determinations — they stick to the names of VAN BENEDEN. I am trying to ascertain from the literature which of those names should be replaced by others.

Of the following Pinnipedia remains have been found in our country.

† PINNIPEDIA.

Name:	Locality:	Remains found:
1. Monotherium affinis Van Beneden.	Wiegerink quarry.	Calcaneus.
2. Monotherium aberratum Van Beneden.	„ „	1 Metacarpus or metatarsus.
3. Alachterium Cretsii Du Bus.	„ „	Phalanx and left metatarsus of the 5th toe.
4. Phoca vitulinoides Van Ben.	„ „	A fragm. of humerus and a piece of the radius.
5. Palaeophoca? Nysti Van Ben.	„ „	Tooth.
6. Phocanella minor Van Ben	„ „	Fragm. of femur.
7. Gryphoca similis? Van Ben.	Meddeho near Winterswijk.	Calcaneus.

Compared with the remains of † Cetacea, the remains of † Pinnipedia are far less significant. It is striking that I have not met with any remains of † Pinnipedia from the Needsche Berg.

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Mathematics. — *"Weights of the most probable values of the Unknowns in the case of Direct Conditioned Observations".* By Prof. M. J. VAN UVEN. (Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of October 30, 1926).

In adjusting direct conditioned observations, the reliableness of the "solutions", i. e. of the values obtained by adjustment, is indicated by their weights.

In the following paper we propose deriving for these weights an expression which gives them in a closed form as a function of the data, and which moreover holds good under an arbitrary number of conditions.

The quantities observed (m in number) will be designated by $x, y, z, \ldots$; the observed values may be $\xi, \eta, \zeta, \ldots$, resp., their weights $g_\xi, g_\eta, g_\zeta, \ldots$

For simplification's sake we will assume that these m quantities $x, y, z, \ldots$ must satisfy a priori μ linear conditions:

$$\alpha_j\, x + \beta_j\, y + \gamma_j\, z + \ldots = \varkappa_j \qquad j = 1, 2, \ldots \mu, \quad \mu < m \quad . \quad . \quad (1)$$

We form the differences

$$\varkappa_j - (\alpha_j\, \xi + \beta_j\, \eta + \gamma_j\, \zeta + \ldots) = \varkappa_j - [\alpha_j\, \xi] = V_j\,, \quad j = 1, 2, \ldots \mu \quad (2)$$

where [ ] denotes a summation over the variables $x, y, z, \ldots$. Let $X, Y, Z, \ldots$ be m provisionally assumed comparative values for $x, y, z, \ldots$, which, by agreement, satisfy the μ conditions, so that

$$[\alpha_j\, X] = \varkappa_j \qquad j = 1, 2, \ldots \mu,$$

Then, by forming the differences

$$\xi - X = v_x\,, \quad \eta - Y = v_y\,, \quad \zeta - Z = v_z\,, \ldots \quad . \quad . \quad . \quad (3)$$

we have, according to (2):

$$[\alpha_j\, v_x] = -V_j \qquad j = 1, 2, \ldots \mu. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We next consider those comparative values $X, Y, Z, \ldots$ as the most probable values for $x, y, z, \ldots$, for which $[g_\xi\, v_x\, v_x]$ takes the least value allowed by the conditions.

Then the equation $[g_\xi\, v_x\, dv_x] = 0$ must be dependent on the μ equations $[\alpha_j\, dv_x] = 0$ $(j = 1, \ldots \mu)$, whence

$$[g_\xi\, v_x\, dv_x] \equiv \sum_{j=1}^{\mu} \lambda_j\, [\alpha_j\, dv_x]\,;$$

here the λ_j are multiplicators to be determined; the summation sign Σ is used here (and will be used also in future) to designate a summation over the μ conditions. Thus the sum Σ runs always from 1 to μ.

Now we have, as a consequence of the above identity:

$$g_\xi \, v_x = \Sigma \, \lambda_j \, \alpha_j \, , \quad g_\eta \, v_y = \Sigma \, \lambda_j \, \beta_j \, , \quad g_\zeta \, v_z = \Sigma \lambda_j \, \gamma_j \, , \ldots m \text{ equations} \qquad (5)$$

and the μ equations already found:

$$[\alpha_j \, v_x] = - V_j \qquad j = 1, \ldots \mu \quad \ldots \ldots \ldots \quad (4)$$

hence altogether $m + \mu$ equations to determine the $m + \mu$ unknowns $v_x, v_y, v_z, \ldots, \lambda_1, \lambda_2, \ldots \lambda_\mu$.

The usual solution runs as follows:

From (4) and (5) we derive the μ equations:

$$\sum_{j=1}^{\mu} \lambda_j \left[\frac{\alpha_j \, \alpha_k}{g_\xi} \right] = - V_k \, , \qquad k = 1, \ldots \mu$$

or, putting for the sake of abbreviation:

$$\left[\frac{\alpha_j \, \alpha_k}{g_\xi} \right] = s_{jk}, \qquad (s_{jk} = s_{kj}) \quad \ldots \ldots \ldots \quad (6)$$

$$\sum_{j=1}^{\mu} s_{kj} \, \lambda_j = - V_k \, , \qquad k = 1, \ldots \mu . \quad \ldots \ldots \quad (7)$$

These μ equations determine the μ multiplicators λ_j.

Denoting the solution of these equations by $\overline{\lambda}_j$, and representing the values of $v_x, v_y, v_z, \ldots$, corresponding with them, according to (5), by $u_x, u_y, u_z, \ldots$, we have:

$$u_x = \frac{1}{g_\xi} \Sigma \, \alpha_j \, \overline{\lambda}_j \, ; \quad u_y = \frac{1}{g_\eta} \Sigma \, \beta_j \, \overline{\lambda}_j \, , \quad u_z = \frac{1}{g_\zeta} \Sigma \, \gamma_j \, \overline{\lambda}_j \, , \ldots \quad . \quad (8)$$

the most probable values of $x, y, z, \ldots$ being

$$\overline{x} = \xi - u_x \, , \quad \overline{y} = \eta - u_y \, , \quad \overline{z} = \zeta - u_z \, \ldots \quad \ldots \quad (9)$$

and $[g_\xi \, u_x \, u_x]$ being the least value which $[g_\xi \, v_x \, v_x]$ may assume, so far as the conditions allow.

The mean (true) error σ of the unity of weight follows from

$$\sigma^2 = \frac{[g_\xi \, u_x \, u_x]}{\mu} \quad \ldots \ldots \ldots \ldots \quad (10)$$

The sum $[g_\xi \, u_x \, u_x]$ may also be expressed directly into the data:

$$[g_\xi \, u_x \, u_x] = \sum_k \sum_j \left[g_\xi \cdot \frac{\alpha_k \, \overline{\lambda}_k}{g_\xi} \cdot \frac{\alpha_j \, \overline{\lambda}_j}{g_\xi} \right] = \sum_k \sum_j \left[\frac{\alpha_k \, \alpha_j}{g_\xi} \, \overline{\lambda}_k \, \overline{\lambda}_j \right] =$$

$$= \sum_k \sum_j \left[\frac{\alpha_k \, \alpha_j}{g_\xi} \right] \overline{\lambda}_k \, \overline{\lambda}_j = \sum_k \sum_j s_{kj} \, \overline{\lambda}_k \, \overline{\lambda}_j$$

(see (8) and (6)), or, since $\overline{\lambda}_j$, being the solution of (7), satisfies

$$\sum_j s_{kj} \, \overline{\lambda}_j = - V_k \, ,$$

$$[g_\xi \, u_x \, u_x] = - \sum_k V_k \, \overline{\lambda}_k \, .$$

Representing the determinant $|s_{jk}| = \begin{vmatrix} s_{11}, & s_{12}, & \dots & s_{1\mu} \\ \vdots & & & \\ s_{1\mu}, & s_{2\mu}, & \dots & s_{\mu\mu} \end{vmatrix}$ by S, and the minor (algebraic complement) of the element s_{jk} by S_{jk} (whence $S = \sum\limits_j s_{jk} S_{jk}$, $0 = \sum\limits_j s_{jk} S_{jl}$ $(l \neq k)$), we have

$$\bar{\lambda}_k = \frac{-\sum\limits_j S_{jk} V_j}{S},$$

hence

$$[g_\xi \, u_x \, u_x] = \frac{\sum\limits_k \sum\limits_j S_{jk} V_j V_k}{S} = -\frac{1}{S} \begin{vmatrix} s_{11}, & \dots & s_{1\mu}, & V_1 \\ \vdots & & & \\ s_{1\mu}, & \dots & s_{\mu\mu}, & V_\mu \\ V_1, & \dots & V_\mu, & 0 \end{vmatrix},$$

or, putting for the sake of abbreviation:

$$\begin{vmatrix} s_{11}, & \dots & s_{1\mu}, & q_1 \\ \vdots & & \vdots & \vdots \\ s_{1\mu}, & \dots & s_{\mu\mu}, & q_\mu \\ p_1, & \dots & p_\mu, & r \end{vmatrix} = \begin{vmatrix} s_{jk} & q_j \\ p_k & r \end{vmatrix}, \quad \dots \dots \dots \quad (11)$$

$$[g_\xi \, u_x \, u_x] = -\frac{1}{S} \begin{vmatrix} s_{jk}, & V_j \\ V_k, & 0 \end{vmatrix} \quad \dots \dots \dots \quad (12)$$

The uncertainty of the "solutions" $\bar{x}, \bar{y}, \bar{z}, \dots$ (see (9)) depends, in the last instance, on the uncertainty of the observed values $\xi, \eta, \zeta, \dots$; these latter have the weights $g_\xi, g_\eta, g_\zeta, \dots$, thus the mean errors:

$$\sigma_\xi = \frac{\sigma}{\sqrt{g_\xi}}, \quad \sigma_\eta = \frac{\sigma}{\sqrt{g_\eta}}, \quad \sigma_\zeta = \frac{\sigma}{\sqrt{g_\zeta}}, \dots$$

If we imagine that, in eventually repeating the series of observations, the observed values $\xi, \eta, \zeta, \dots$ undergo the variations $\Delta\xi, \Delta\eta, \Delta\zeta, \dots$ respectively, then the mean square of $\Delta\xi$ (represented by $\overline{\Delta\xi^2}$) is nothing else than the square of the mean error of ξ, etc., in other words:

$$\overline{\Delta\xi^2} = \frac{\sigma^2}{g_\xi}, \quad \overline{\Delta\eta^2} = \frac{\sigma^2}{g_\eta}, \quad \overline{\Delta\zeta^2} = \frac{\sigma^2}{g_\zeta}, \dots \dots \dots \quad (13)$$

the mutual independency of the observed values $\xi, \eta, \zeta, \dots$ having as a consequence that the mean products, two by two, of the variations $\Delta\xi, \Delta\eta, \Delta\zeta, \dots$ are zero, so that

$$\overline{\Delta\xi \, . \, \Delta\eta} = 0, \quad \overline{\Delta\xi \, . \, \Delta\zeta} = 0, \dots, \overline{\Delta\eta \, . \, \Delta\zeta} = 0 \text{ etc.} \quad \dots \quad (14)$$

In consequence of the variations $\Delta\xi, \Delta\eta, \Delta\zeta, \dots$, the V_j undergo (according to (2)) the variations

$$\Delta V_j = -[\alpha_j \, \Delta\xi] = -(\alpha_j \, \Delta\xi + \beta_j \, \Delta\eta + \gamma_j \, \Delta\zeta + \dots).$$

The variations $\Delta\lambda_k$ of $\bar{\lambda}_k$, deriving from these ΔV_j, satisfy (see (7))

$$\sum s_{kj} \, \Delta\lambda_j = -\Delta V_k \, . \qquad k = 1, \dots \mu \quad \dots \dots \quad (15)$$

Further, from

$$u_x = \frac{1}{g_\xi}\sum_j a_j\,\bar{\lambda}_j = \xi - \bar{x} : \quad . \quad . \quad . \quad . \quad . \quad . \quad (8),\ (9)$$

follows

$$\sum \frac{a_j}{g_\xi}\,\Delta\lambda_j = \Delta\xi - \Delta\bar{x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

We now multiply the μ equations (15) and the equation (16) by $\Delta\xi$. Then, taking the mean value, we obtain (by (13) and (14))

$$\sum_j s_{kj}\,\overline{\Delta\lambda_j\,.\,\Delta\xi} = -\overline{\Delta V_k\,.\,\Delta\xi} = +(a_k\,\overline{\Delta\xi^2} + \beta_k\,\overline{\Delta\xi\,.\,\Delta\eta} + \gamma_k\,\overline{\Delta\xi\,.\,\Delta\zeta} + \dots)$$

$$= \frac{a_k}{g_\xi}\,\sigma^2 \qquad k = 1, \dots \mu$$

$$\sum \frac{a_j}{g_\xi}\,\overline{\Delta\lambda_j\,.\,\Delta\xi} = \overline{\Delta\xi^2} - \overline{\Delta\bar{x}\,.\,\Delta\xi} = \frac{\sigma^2}{g_\xi} - \overline{\Delta\bar{x}\,.\,\Delta\xi}.$$

By eliminating the μ variables $\overline{\Delta\lambda_j\,.\,\Delta\xi}$ from these $\mu + 1$ equations and using the notation (11), we arrive at

$$\begin{vmatrix} s_{kj}, & \dfrac{a_k}{g_\xi}\,\sigma^2 \\ \dfrac{a_j}{g_\xi}, & \dfrac{\sigma^2}{g_\xi} - \overline{\Delta\bar{x}\,.\,\Delta\xi} \end{vmatrix} = 0,$$

or

$$\begin{vmatrix} s_{kj}, & \dfrac{a_k}{g_\xi}\,\sigma^2 \\ \dfrac{a_j}{g_\xi}, & \dfrac{\sigma^2}{g_\xi} \end{vmatrix} - \begin{vmatrix} s_{kj}, & 0 \\ \dfrac{a_j}{g_\xi}, & \overline{\Delta\bar{x}\,.\,\Delta\xi} \end{vmatrix} = 0,$$

or

$$\frac{\sigma^2}{g_\xi}\begin{vmatrix} s_{kj}, & \dfrac{a_k}{g_\xi} \\ a_j\ , & 1 \end{vmatrix} - S\,.\,\overline{\Delta\bar{x}\,.\,\Delta\xi} = 0,$$

whence

$$\overline{\Delta\bar{x}\,.\,\Delta\xi} = \frac{1}{S}\,.\,\frac{\sigma^2}{g_\xi}\,.\begin{vmatrix} s_{kj}, & \dfrac{a_k}{g_\xi} \\ a_j\ , & 1 \end{vmatrix} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

In the same manner we obtain, by multiplying the μ equations (15) and the equation (16) by $\Delta\eta$, and then taking the mean,

$$\sum_j s_{kj}\,\overline{\Delta\lambda_j\,.\,\Delta\eta} = -\overline{\Delta V_k\,.\,\Delta\eta} = +(a_k\,\overline{\Delta\eta\,.\,\Delta\xi} + \beta_k\,\overline{\Delta\eta^2} + \gamma_k\,\overline{\Delta\eta\,.\,\Delta\zeta} + \dots)$$

$$= \frac{\beta_k}{g_\eta}\,\sigma^2 \qquad k = 1, \dots \mu$$

$$\sum_j \frac{a_j}{g_\xi}\,\overline{\Delta\lambda_j\,.\,\Delta\eta} = \overline{\Delta\xi\,.\,\Delta\eta} - \overline{\Delta\bar{x}\,.\,\Delta\eta} = -\overline{\Delta\bar{x}\,.\,\Delta\eta}.$$

From these $\mu+1$ equations we derive by eliminating the μ variables $\overline{\Delta\lambda_j\cdot\Delta\eta}$:

$$\begin{vmatrix} s_{kj}, & \frac{\beta_k}{g_\eta}\sigma^2 \\ \frac{a_j}{g_\xi}, & 0-\overline{\Delta\bar{x}\cdot\Delta\eta} \end{vmatrix}=0,$$

or

$$\begin{vmatrix} s_{kj}, & \frac{\beta_k}{g_\eta}\sigma^2 \\ \frac{a_j}{g_\xi}, & 0 \end{vmatrix} - \begin{vmatrix} s_{kj}, & 0 \\ \frac{a_j}{g_\xi}, & \overline{\Delta\bar{x}\cdot\Delta\eta} \end{vmatrix}=0,$$

or

$$\frac{\sigma^2}{g_\xi}\begin{vmatrix} s_{kj}, & \frac{\beta_k}{g_\eta} \\ a_j, & 0 \end{vmatrix} - S\cdot\overline{\Delta\bar{x}\,\Delta\eta}=0,$$

whence

$$\overline{\Delta\bar{x}\cdot\Delta\eta}=\frac{1}{S}\cdot\frac{\sigma^2}{g_\xi}\cdot\begin{vmatrix} s_{kj}, & \frac{\beta_k}{g_\eta} \\ a_j, & 0 \end{vmatrix} \quad \ldots\ldots \quad (18)$$

Likewise we find

$$\overline{\Delta\bar{x}\cdot\Delta\zeta}=\frac{1}{S}\cdot\frac{\sigma^2}{g_\xi}\cdot\begin{vmatrix} s_{kj}, & \frac{\gamma_k}{g_\zeta} \\ a_j, & 0 \end{vmatrix} \quad \ldots\ldots \quad (18\text{ bis})$$

etc.

We next multiply (15) by $\Delta\bar{x}$ and take the mean; so we obtain (replacing the index k by i):

$$\sum_j s_{ij}\,\overline{\Delta\lambda_j\cdot\Delta\bar{x}}=-\overline{\Delta V_i\cdot\Delta\bar{x}}=+(a_i\,\overline{\Delta\bar{x}\cdot\Delta\xi}+\beta_i\,\overline{\Delta\bar{x}\cdot\Delta\eta}+$$
$$+\gamma_i\,\overline{\Delta\bar{x}\cdot\Delta\zeta}+\ldots),\ i=1,\ldots\mu$$

or, on account (17), (18), (18 bis) etc.

$$\sum_j s_{ij}\overline{\Delta\lambda_j\cdot\Delta\bar{x}}=\frac{1}{S}\cdot\frac{\sigma^2}{g_\xi}\cdot\left\{a_i\begin{vmatrix} s_{kj}, & \frac{a_k}{g_\xi} \\ a_j, & 1 \end{vmatrix}+\beta_i\begin{vmatrix} s_{kj}, & \frac{\beta_k}{g_\eta} \\ a_j, & 0 \end{vmatrix}+\gamma_i\begin{vmatrix} s_{kj}, & \frac{\gamma_k}{g_\zeta} \\ a_j, & 0 \end{vmatrix}+\ldots\right\}$$

$$=\frac{1}{S}\cdot\frac{\sigma^2}{g_\xi}\cdot\begin{vmatrix} s_{kj}, & \left[\frac{a_k\,a_i}{g_\xi}\right] \\ a_j, & a_i \end{vmatrix}=\frac{1}{S}\cdot\frac{\sigma^2}{g_\xi}\cdot\begin{vmatrix} s_{kj}, & s_{ki} \\ a_j, & a_i \end{vmatrix},\ i=1,\ldots\mu$$

or

$$\sum_j s_{ij}\,\overline{\Delta\lambda_j\,.\,\Delta\bar{x}}=\frac{1}{S}\cdot\frac{\sigma^2}{g_\xi}\cdot\begin{vmatrix} s_{11},\ldots, s_{1i},\ldots, s_{1\mu}, & s_{1i}\\ \vdots \qquad \vdots & \\ s_{\mu 1},\ldots, s_{\mu i},\ldots, s_{\mu\mu}, & s_{\mu i}\\ \alpha_1,\ldots,\alpha_i,\ldots,\alpha_\mu, & \alpha_i\end{vmatrix}\equiv 0 \qquad i=1,\ldots\mu$$

The determinant $|s_{ij}|=S$ of the μ homogeneous equations

$$\sum_j s_{ij}\,\overline{\Delta\lambda_j\,.\,\Delta\bar{x}}=0 \qquad i=1,\ldots\mu$$

which we obtain in this way, being different from zero, we have separately

$$\overline{\Delta\lambda_j\,.\,\Delta\bar{x}}=0. \qquad j=1,\ldots\mu \quad \ldots\ldots\ldots \quad (19)$$

Multiplying at last the equation (16) by $\Delta\bar{x}$ and then taking the mean, we find

$$\overline{\Delta u_x\,.\,\Delta\bar{x}}=\sum\frac{\alpha_j}{g_\xi}\,\overline{\Delta\lambda_j\,.\,\Delta\bar{x}}=\overline{\Delta\xi\,.\,\Delta\bar{x}}-\overline{\Delta\bar{x}^2}$$

thus, by (19),

$$\overline{\Delta u_x\,.\,\Delta\bar{x}}=\overline{\Delta\xi\,.\,\Delta\bar{x}}-\overline{\Delta\bar{x}^2}=0 \quad \ldots\ldots \quad (20)$$

or, on account of (17),

$$\overline{\Delta\bar{x}^2}=\overline{\Delta\xi\,.\,\Delta\bar{x}}=\frac{1}{S}\cdot\frac{\sigma^2}{g_\xi}\cdot\begin{vmatrix} s_{kj} & \dfrac{\alpha_k}{g_\xi}\\ \alpha_j & 1\end{vmatrix} \quad \ldots\ldots \quad (21)$$

Now, $\overline{\Delta\bar{x}^2}$ being nothing but the square of the mean error $\sigma_{\bar{x}}$ of $\bar{x}$, we have

$$\sigma_{\bar{x}}^2=\frac{1}{S}\cdot\frac{\sigma^2}{g_\xi}\cdot\begin{vmatrix} s_{kj}, & \dfrac{\alpha_k}{g_\xi}\\ \alpha_j, & 1\end{vmatrix} \quad \ldots\ldots\ldots \quad (22)$$

We shall moreover put this latter determinant into another form. In

$$\begin{vmatrix} s_{kj}, & \dfrac{\alpha_k}{g_\xi}\\ \alpha_j, & 1\end{vmatrix}=\begin{vmatrix} s_{11},\ldots, s_{1j},\ldots, s_{1\mu}, & \alpha_1:g_\xi\\ \vdots \qquad \vdots \qquad \vdots & \vdots\\ s_{k1},\ldots, s_{kj},\ldots, s_{k\mu}, & \alpha_k:g_\xi\\ \vdots \qquad \vdots \qquad \vdots & \vdots\\ s_{\mu 1},\ldots, s_{\mu j},\ldots, s_{\mu\mu}, & \alpha_\mu:g_\xi\\ \alpha_1,\ldots,\alpha_j,\ldots,\alpha_\mu, & 1\end{vmatrix}$$

we take from the 1st column α_1 times the last column

⋮

,, j^{th} ,, α_j ,, ,, ,, ,,

⋮

,, μ^{th} ,, α_μ ,, ,, ,, ,, .

Then we retain for the element of the j^{th} column and the k^{th} row:

$$s_{kj} - \frac{\alpha_j\,\alpha_k}{g_\xi} = \left[\frac{\alpha_k\,\alpha_j}{g_\xi}\right] - \frac{\alpha_k\,\alpha_j}{g_\xi} = \frac{\beta_k\,\beta_j}{g_\eta} + \frac{\gamma_k\,\gamma_j}{g_\zeta} + \ldots = a_{kj}\,. \quad (23)$$

the j^{th} element of the last row becoming zero $(j = 1, \ldots \mu)$. Representing the determinant $|a_{kj}|$ by A, we obtain

$$\begin{vmatrix} s_{kj}\,, & \dfrac{\alpha_k}{g_\xi} \\ \alpha_j\,, & 1 \end{vmatrix} = \begin{vmatrix} a_{kj}\,, & \dfrac{\alpha_k}{g_\xi} \\ 0\,, & 1 \end{vmatrix} = |a_{kj}| = A.$$

So we find

$$\sigma_{\bar{x}}^2 = \frac{A}{S} \cdot \frac{\sigma^2}{g_\xi}$$

and for the weight $g_{\bar{x}}$ of $\bar{x}$:

$$g_{\bar{x}} = \frac{S}{A} \cdot g_\xi\,.$$

Putting in a similar manner:

$$s_{kj} - \frac{\beta_j\,\beta_k}{g_\eta} = \left[\frac{\alpha_k\,\alpha_j}{g_\xi}\right] - \frac{\beta_k\,\beta_j}{g_\eta} = \frac{\alpha_k\,\alpha_j}{g_\xi} + \frac{\gamma_k\,\gamma_j}{g_\zeta} + \ldots = b_{kj}\,. \quad (23\text{ bis})$$

$$s_{kj} - \frac{\gamma_j\,\gamma_k}{g_\zeta} = \left[\frac{\alpha_k\,\alpha_j}{g_\xi}\right] - \frac{\gamma_k\,\gamma_j}{g_\zeta} = \qquad\qquad = c_{kj}\,. \quad (23\text{ ter})$$

etc.,
and further:

$$|b_{kj}| = B \quad , \quad |c_{kj}| = C, \text{ etc.,}$$

we arrive at last at:

$$\sigma_{\bar{x}}^2 = \frac{A}{S} \cdot \frac{\sigma^2}{g_\xi} \quad , \quad \sigma_{\bar{y}}^2 = \frac{B}{S} \cdot \frac{\sigma^2}{g_\eta} \quad , \quad \sigma_{\bar{z}}^2 = \frac{C}{S} \cdot \frac{\sigma^2}{g_\zeta}, \text{ etc.,} \quad . \quad . \quad (24)$$

or

$$g_{\bar{x}} = \frac{S}{A} \cdot g_\xi \quad , \quad g_{\bar{y}} = \frac{S}{B} \cdot g_\eta \quad , \quad g_{\bar{z}} = \frac{S}{C} \cdot g_\zeta\,, \text{ etc.} \quad . \quad . \quad . \quad . \quad (25)$$

Thus we have expressed the weights of the solutions in a closed form into the data g_ξ, g_η, $g_\zeta, \ldots$; α_j, β_j, $\gamma_j, \ldots$ $(j = 1, \ldots \mu)$

If there is given, in particular, but one condition

$$\alpha x + \beta y + \gamma z + \ldots = \varkappa$$

so that $\mu = 1$, then we have

$$S = \left[\frac{\alpha\,\alpha}{g_\xi}\right], \; A = \left[\frac{\alpha\,\alpha}{g_\xi}\right] - \frac{\alpha\,\alpha}{g_\xi} = \frac{\beta\,\beta}{g_\eta} + \frac{\gamma\,\gamma}{g_\zeta} + \ldots,$$

$$B = \left[\frac{\alpha\,\alpha}{g_\xi}\right] - \frac{\beta\,\beta}{g_\eta} = \frac{\alpha\,\alpha}{g_\xi} + \frac{\gamma\,\gamma}{g_\zeta} + \ldots, \quad C = \ldots, \text{ etc.,}$$

thus

$$\sigma_{\underline{x}}^{2}=\frac{\sigma^2}{g_\xi}\cdot\frac{\frac{\beta\beta}{g_\eta}+\frac{\gamma\gamma}{g_\zeta}+\dots}{\frac{\alpha\alpha}{g_\xi}+\frac{\beta\beta}{g_\eta}+\frac{\gamma\gamma}{g_\zeta}+\dots},\quad \sigma_{\underline{y}}^{2}=\frac{\sigma^2}{g_\eta}\cdot\frac{\frac{\alpha\alpha}{g_\xi}+\frac{\gamma\gamma}{g_\zeta}+\dots}{\frac{\alpha\alpha}{g_\xi}+\frac{\beta\beta}{g_\eta}+\frac{\gamma\gamma}{g_\zeta}+\dots},\quad \sigma_{\underline{z}}^{2}=\dots,\text{etc.} \qquad (24\text{bis})$$

The determinants $S, A, B, C, \dots$ may yet be put into another form. Of the m variables $x, y, z, \dots,$ represented by $g_\xi, g_\eta, g_\zeta, \dots$ and by $\alpha_j, \beta_j, \gamma_j, \dots,$ we consider the combinations μ by μ. Be $x, z, \dots t$ $(g_\xi, g_\zeta, \dots g_\tau;\ \alpha_j, \gamma_j, \dots \theta)$ such a combination.

Then we may form determinants such as

$$\triangle(x, z, \dots t)=\begin{vmatrix} \alpha_1, & \gamma_1, & \dots & \theta_1 \\ \alpha_2, & \gamma_2, & \dots & \theta_2 \\ \vdots & & & \\ \alpha_\mu, & \gamma_\mu, & \dots & \theta_\mu \end{vmatrix}$$

According to the theory of determinants, we may write S as follows:

$$S=|s_{kj}|=\left|\left[\frac{\alpha_k\,\alpha_j}{g_\xi}\right]\right|=\Sigma\,\frac{\triangle^2(x, z, \dots t)}{g_\xi\cdot g_\zeta\cdots g_\tau}\,. \quad . \quad . \quad . \quad (27)$$

where the sum Σ runs over all the $C_\mu(m)=\dfrac{m!}{\mu!\,(m-\mu)!}$ combinations μ by μ of the m elements $x, y, z, \dots$.

In the same manner we may also reduce the determinant A.

Here all the m elements $x, y, z, \dots$ appear, except the element x. With these $m-1$ elements $y, z, \dots$ we can build determinants of the form:

$$\triangle_x(y, z, \dots t)=\begin{vmatrix} \beta_1, & \gamma_1, & \dots & \theta_1 \\ \vdots & & & \\ \beta_\mu, & \gamma_\mu, & \dots & \theta_\mu \end{vmatrix}, \quad . \quad . \quad . \quad . \quad . \quad (28)$$

wherein the elements α_j are always missing.

So we have

$$A=|a_{kj}|=\left|\left[\frac{\alpha_k\,\alpha_j}{g_\xi}\right]-\frac{\alpha_k\,\alpha_j}{g_\xi}\right|=\Sigma_x\,\frac{\triangle_x^2(y, z, \dots t)}{g_\eta\cdot g_\zeta\cdots g_\tau}, \quad . \quad . \quad (29)$$

where the sum Σ_x extends over all the $C_\mu\,(m-1)=\dfrac{(m-1)!}{\mu!\,(m-\mu-1)!}$ combinations μ by μ of the $m-1$ elements $y, z, \dots$ (x absent).

Similarly:

$$B=|b_{kj}|=\Sigma_y\,\frac{\triangle_y^2(x, z, \dots t)}{g_\xi\cdot g_\zeta\cdots g_\tau}\,. \quad . \quad . \quad . \quad . \quad (29\text{ bis})$$

$$C=|c_{kj}|=\Sigma_z\,\frac{\triangle_z^2(x, y, \dots t)}{g_\xi\cdot g_\eta\cdots g_\tau}\,. \quad . \quad . \quad . \quad . \quad (29\text{ ter})$$

etc.

So the determinants $S, A, B, C, \ldots$ are written as sums of positive terms. The terms of the sum A also appear in the sum S, which contains besides those terms depending upon the element $x(g_\xi, a_j)$. Thus the value A is certainly less than that of S. Likewise $B, C, \ldots$ are altogether less than S.

The fractions $\frac{A}{S}, \frac{B}{S}, \frac{C}{S}, \ldots$ are therefore altogether less than unity, so that the mean errors $\sigma_{\bar{x}}, \sigma_{\bar{y}}, \sigma_{\bar{z}}, \ldots$ of the solutions are less than the mean errors of the respective observations, viz:

$$\sigma_\xi = \frac{\sigma}{\sqrt{g_\xi}}, \quad \sigma_\eta = \frac{\sigma}{\sqrt{g_\eta}}, \quad \sigma_\zeta = \frac{\sigma}{\sqrt{g_\zeta}}, \ldots.$$

thus:

$$\sigma_{\bar{x}} < \sigma_\xi, \quad \sigma_{\bar{y}} < \sigma_\eta, \quad \sigma_{\bar{z}} < \sigma_\zeta, \quad \ldots \ldots \qquad (30)$$

If all the terms of the sum S (27) are nearly equal, then the sums A and S are almost proportional to the numbers of their terms, thus as $C_\mu(m-1)$ to $C_\mu(m)$, that is: as $m-\mu$ to m. In this case the mean errors of the solutions are about $\sqrt{\frac{m-\mu}{m}}$ times as large as the mean errors of the corresponding observations. The larger μ is in comparison to m, the more the solution surpasses the observation in accuracy.

Chemistry. — *"On Double-Salts in the Series of isomorphous Mixed Crystals of Magnesium- and Zinc-sulphate, and on the Occurrence of Chemical Compounds in the Solid State."* By H. G. K. WESTENBRINK. (Communicated by Prof. F. M. JAEGER.)

(Communicated at the meeting of October 30, 1926).

§ 1. According to HOLLMANN's investigations [1], *two* double-salts: $2\,MgSO_4, ZnSO_4, 21\,H_2O$ and $MgSO_4, ZnSO_4, 14\,H_2O$, would be inclosed in the continuous series of mixed crystals, which are formed in all proportions on crystallisation of mixed solutions of *magnesium* and *zinc-sulphate* in water. To this view he was led by the results of his measurements of the vapour-tensions of these mixed crystals, executed after the so-called "indirect" method, which consists in the determination of the concentration of mixtures of water and sulphuric acid, if these mixtures were in equilibrium with the hydrates of definite composition, when put together in an exsiccator.

In the curve, representing the vapour-tension as a function of the composition of the mixed crystals, HOLLMANN observed two discontinuities, which, according to him, were situated at the stoechiometric proportions: $Mg : Zn = 1 : 1$ and $2 : 1$. As in general, from earlier experiments it was seen, that the vapour-tension varies continuously with the composition of the solid phase, he drew the conclusion that the discontinuities observed must be considered to be the points of intersection of three continuous vapour tension-curves, which refer successively to a series of mixed crystals between $MgSO_4, 7\,H_2O$ and the first mentioned double-salt, to such between both double-salts indicated above, and to such between the second double-salt and pure $ZnSO_4, 7\,H_2O$. Later-on he tried to corroborate these conclusions by fixing the particular temperatures of decomposition of the mixed crystals into *hexa*hydrates and water, applying the dilatometric method [2]). If these temperatures be graphically represented in function of the chemical composition, they form again a curve with two discontinuities, situated at the same stoechiometric proportions as mentioned above. HOLLMANN [3]), following the method of VAN RIJN VAN ALKEMADE [4]) and BAKHUIS ROOZEBOOM [5]), deduced three types of temperature-concentration-curves for the case of the decomposition of a mixed crystal with definite content of crystal-water into a mixed crystal with a smaller number of water-molecules and a saturated solution. The three types deduced by him are: 1st. The curve rises continually from 100 % A to 100 % B; 2nd. the curve shows a minimum; 3rd. the curve shows a maximum. The two discontinuities in the curve relating to the mixed crystals $Mg(Zn)SO_4, 7\,H_2O$ are, according to HOLLMANN, again the points of intersection of three continuous curves. Indeed, such a shape of the curve, as really observed, might be expected beforehand, if double-salts were present in the series. However, several objections can be made with respect to his way of experimenting. One could put the question, for instance, whether the same hydrate is always formed from the heptahydrate? Whether this lower hydrate always and in all proportions forms mixed crystals? Whether the equilibria set in rapidly enough, to allow the appliance of the dilatometric method? Etc. Moreover, the author has drawn his curves rather arbitrarily through the 19 points observed. It can be doubted, whether the tendency to find his compound at the proportions: $MgSO_4 : ZnSO_4 = 1 : 1$ and $2 : 1$, has not had a real influence on his interpretation of the facts? It is, moreover, very difficult to answer the question, whether the minima observed are to be considered as real discontinuities in his curve; etc.

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[1]) R. HOLLMANN, Zeits. f. phys. Chemie, **37**, 193, (1901).

[2]) A. C. VAN RIJN VAN ALKEMADE, Zeits. f. phys. Chemie, **11**, 289, (1893).

[3]) H. W. BAKHUIS ROOZEBOOM, Zeitschr. phys. f. Chemie, **30**, 385, (1899).

[4]) R. HOLLMANN, Zeits. f. phys. Chemie, **40**, 577, (1902).

[5]) R. HOLLMANN, Zeits. f. phys. Chemie, **40**, 561, (1902).

Later-on BARCHET [1]) made a series of solubility-measurements of the same salts when forming mixed crystals. In his results he could not see a confirmation of the occurrence of HOLLMANN's two compounds. The last author [2]) again emphazised, that BARCHET's interpretation of the observed facts was to be considered as erroneous, and that, on the contrary, from his results the existence of the compounds might be deduced. Here HOLLMANN again makes use of VAN RIJN VAN ALKEMADE's method, who deduced the solubility-curve for two salts and for two salts and two double-salts, with or without water of crystallisation, making use of GIBBS' graphical representation of the ζ-function. However, VAN RIJN VAN ALKEMADE did not draw the curve which must be present if mixed crystals form the solid phase; also the simultaneous occurrence of mixed crystals and double salts is left completely out of consideration by him. For this last mentioned case, HOLLMANN deduces a curve, which agrees with that deduced from BARCHET's observations. Theoretically, the solubility-curve is found by drawing the tangents to the ζ-curve of the mixed crystals and the ζ-surface of the saturated solutions: the points of touching at the last surface form together the desired solubility-curve. But the accurate shape of both ζ-functions being not known, it is impossible to get convinced of the fact, that a curve, agreeing in shape with that determined experimentally, should not as well be valid for the case that only mixed crystals, and no compounds whatsoever, represent the solid phase of the system.

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[1]) E. BARCHET, N. Jahrb. f. Miner., etc. Beil. Bnd. 18, 377, (1904).

[2]) R. HOLLMANN, Centr Bl. f. Miner., (1904), 513.

It seems evident from the foregoing, that little hope is left to settle these questions by a repetition of HOLLMANN's and BARCHET's experiments. Quite independently from this, the problem of the possible occurrence of these compounds may, however, also be treated by the aid of the results of the structure-theory of the solid state. Then it will be necessary to ascertain in the first place, how under these circumstances must be understood the expression solid "compound", as contrasted by the conception of "mixed crystal".

§ 2. In the first place is it, therefore, necessary to remember, what the ROENTGENographic investigations have taught us about the structures of mixed crystals in general.

Mixed crystals may, à priori, be conceived as being built up in three fundamental ways:

1st. They represent heterogeneous conglomerates of very small, crystalline parts of the components.

2nd. They are homogeneous, or quasi-homogeneous, crystals, the constituent kinds of atoms or atom-groups substituting each other in the regular structure in a completely hasardous way.

3rd. They are homogeneous crystals, in which the substituting atoms, replace each other in a perfectly regular way.

The way of structure as mentioned sub 1°, which is, already from the point of view of the phase-rule, highly improbable, is not confirmed by any result of the ROENTGEN-analysis.

It is true, that the regular distribute of the atoms in mixed crystals, as mentioned sub 3rd, is defended more in particulars by TAMMANN [1]). This view was expressed by him in trying to explain the occurrence of apparent limits of concentration in such series of mixed crystals, at which limits their resistance against chemical attack appeared suddenly much greater than before or afterwards. Such cases were found in the case of mixed crystals between metals, or such salts as $NaCl$ and $AgCl$. As a result of many observations made in his laboratory, it seemed to be evident, that, if in the case of these cubic mixed crystals their concentration, expressed in molecular fractions of the whole, the composition corresponded to $^1/_8$ mol. of the nobler metal or to a multiple $^n/8$ of it, — suddenly an increase of resistance in chemical respect occurred; in the case of syncrystallizing metals, simultaneously a sudden change in potential with respect to a suitable electrolyte could be observed. Doubt has rightly arisen, whether the limits indicated here, are really situated at $^n/8$ molecules so exactly as TAMMANN believes; but the occurrence of definite limits of maximum chemical resistance seems to be sure, as also other experimenters, quite independently of him, have found analogous facts. It is worth remarking, that MASING [1]) and BORELIUS [2]) succeeded in deducing theoretically the possible occurrence of such limits in a series of mixed crystals, if it was assumed beforehand, that the way of arrangement and substitution of the "vicarious" atoms or atoms-groups in such mixed crystals is completely haphazardous. But the limits calculated by them are *not* situated at exactly $^n/_8$ molecules.

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[1]) G. TAMMANN, Zeits. f. anorg. Chem., **107**, 1, (1919).

§ 3. TAMMANN [3]) assumes a real difference between solid compounds and mixed crystals only at higher temperatures, where appreciable "diffusion" can take place: from a mixed crystal both species of atoms will then diffuse into an outer medium *independently* from each other, while from a crystallized compound they will diffuse together and only in a fixed proportion.

However, with the view, mentioned above, concerning the regular distribution of the substituting atoms in a mixed crystal, TAMMANN comes in conflict with the general structure-theory of solid matter, as may be seen from the following considerations.

A "regular" distribution, as meant by TAMMANN, can have no other significance in this connection, than that also a mixed crystal is considered to be an interpenetration of "homogeneous discontinua", in which each point is surrounded by the other points in an identical way; "identical" here being understood in the sense of "congruent" or "equal to its mirror-image". Therefore, the atoms must be arranged in this case in such a way, as is described by means of one of the 230 possible space-groups. But then there must always be present *identical* atoms in *crystallographically-equivalent* positions. In a mixed crystal of a quite arbitrary composition, this is evidently impossible; for to each point of the elementary cell, determined by a definite space-group, correspond a number of $(n—1)$ equivalent points, if n be the number indicating the special degree of equivalence of the point first considered. If one of these n atoms be replaced by another, then the other $(n—1)$ places must be substituted simultaneously by the new atom, if the symmetry-character of the structure will remain preserved. In most of the real "compounds", n equal atoms are situated in such positions, as are characterized by a same degree of equivalence n; sometimes in points, for which the sum of the degrees of equivalence is equal to n. It is, therefore, often observed, that the ratio of the numbers of atoms or atomgroups of a compound, appears to be equal to the ratio of the degrees of equivalence of the positions in the elementary cell, in which places these atoms are situated. Thus e.g. compounds with *three* (or a multiple of three) equal atoms or atom-groups arranged round a central atom, often appear to be *tri*gonal or

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[1]) G. MASING, Zeits. f. anorg. Chem., **118**, 293, (1922).

[2]) G. BORELIUS, Ann. d. Phys., **74**, 216, (1924).

[3]) G. TAMMANN, Zeits. f. Electrochemie, **28**, 36, (1922).

*hexa*gonal; such with *four* equal atoms or atom-groups often appear to be *tetra*gonal[1]) or *cubic*; etc.

Because the numbers of the different atoms in a chemical compound are always in proportion of simple integers, the structure of the crystals is possible according to a simple scheme. But in mixed crystals, in which *all* mixing proportions of the vicarious atoms or atom-groups are possible, yet for each concentration a structure is imaginable in which the symmetry-relations of one of the space-groups are valid; but, on the other hand, it will often appear necessary in such cases, to distribute *identical* atoms over numerous places which are characterized by different values of their degree of equivalence; moreover, that distribution will be different for each special concentration of the mixed crystal. Also it will be necessary, almost in each case, to assume elementary cells of abnormal size, — the last also necessarily varying with each concentration. This kind of structure of the mixed crystals is so improbable, that this view of it may be quietly left out of consideration here.

No difficulties of this kind arise, however, if an irregular, i. e. *statistical* distribution of the substituting atoms be assumed in a grating, whose fundamental dimensions may be derived in an additive way[2]) from the grating-dimensions of the components of the mixed crystal. VON LAUE[3]) has shown, starting from a set of premisses, that a mixed crystal built up in this way, will give the same, well defined diffraction-images, as the pure components do. In accordance with the additive character of the fundamental dimensions, the interference-lines will be shifted somewhat with respect to the lines met with in the case of the pure components. Although the original symmetry-elements are, properly speaking, no longer present, because of the unequal nature of the constituting atoms, their absence is in no way manifested in the spectrograms obtained, because they manifest themselves in a statistical way in the crystal-symmetry, and consequently also in the external form.

§ 4. However, for a rigorous and exhaustive understanding of what has been said here about the constitution of mixed crystals, it must be remarked in this connection, that the view of the mixed crystal, just as the crystalline pure components, being characterized by a rigorously definite periodicity with a mean value between that of the components, must be understood with the necessary reserve. Recently FRIEDEL[4]) has drawn attention to the fact, that the view, according to which in the mixed crystal a grating with "mean" values for its parameters is be present, may be regarded neither as a logical deduction from the results of the experiment, nor as agreeing with the real state of things. As soon as the well known and generally assumed fact be taken into consideration, that the place of each atom in the structure depends wholly or almost exclusively on the influence of the immediately surrounding atoms, at distances which do not exceed a simple multiple of the parameter-lengths in all directions; and that the far distant particles have, therefore, no appreciable action upon it, — the conclusion mentioned above ceases to be a necessary postulate from the experimental results. For in the case of an irregular, statistical substitution, it may happen in a domain or volume-element with the dimensions of only a few parameter-distances in each direction, that occasionally, for instance, *only* atoms A or *only* atoms B will be present in succession of each other; or that, as in most cases, A and B will occur in very different, quite accidental mutual succession and in different proportions. In a domain, which consists only of atoms A, the parameters can, as a consequence of what was said above, only be those, which are valid in the case of pure A; in a domain, in which only the atoms B occur, these parameters can only have the values valid in the case of pure B; and in all intermediate mixtures of A and B, a finite number of parameter-values will occur, which lie between those of A and B, and depending as well on the proportions of A and B, as on their accidental way of distribution within the volume-element considered. Therefore, the apparently definite chemical constitution of the mixed crystal can only be a statistical "mean" value of all local compositions, which vary from one domain to another. The "homogeneity" of the mixed crystal is thus only a *quasi*-homogeneity, its periodicity a *quasi*-periodicity. Properly speaking, *no* grating whatsoever in the strict sense of the word is present in it any more, showing constant parameters of intermediate, „mean" values. This could only occur, if *all* particles, also those far distant in the structure in its whole extension, — or at least within a sphere whose radius should be very large in comparison with a few parameter-distances, — manifested their influence in fixing the place of the atom originally considered here; — a supposition, which is certainly not true. It can only be proved, that there is a chance considerably greater than all others, that a distribution of the atoms within a microscopical part of the mixed crystal will actually occur, such, that its action on the pencil of ROENTGEN-rays and the incident wave-trains will cause a way of interference, *as if* a grating with a "mean" value of the parameters, determined by the statistical constitution, were really present. The chance for that distribution of atoms is incomparably much greater than that for all other kinds of distribution, deviating from the one mentioned above. It is that circumstance, which causes the behaviour of the mixed crystal with respect to the ROENTGEN-radiation to appear to be that of an apparently real homogeneous discontinuum, with an apparent "grating" of "mean" value, analogous to that of the pure components. However, this phenomenon is in fact a mere illusion: the mixed crystal, as has been said already, does not possess any real grating at all in the strict sense of the structural theory. It is more comparable with a kind of mosaïc, built up by parts of unequal magnitude and different chemical constitution; it is, as said above, *quasi-*homogeneous, *quasi-*periodical, and possesses only a *quasi-*grating as structural fundament.

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[1]) Cf. the numerous instances of this in: P. GROTH, *Elemente der physikalischen und chemischen Krystallographie*, p. 273 and following, (1920).

[2]) This (apparent) additive character was hitherto stated in all cases, in which mixed crystals were studied by means of ROENTGENrays.

[3]) M. VON LAUE, Ann. d. Physik, [4], **56**, 497, (1918).

[4]) G. FRIEDEL, Compt. rend. Paris, **182**, 741, (1926).

§ 5. Only in the case of some mixed crystals with very simple mixing proportions, an atomic distribution as TAMMANN supposes, would be possible, although it is by no means a necessary one. Because of the un-equal nature of the constituent components, the symmetry will, in the case of an analogous structure like that of the components, necessarily be of a *lower* degree than that of those components. In the ROENTGEN-spectograms a greater number of diffraction-lines would, therefore, be observed than in the corresponding spectograms of the pure components. Such crystals would appear, therefore, built up after a totally different scheme, in comparison with the other members of the series. Such crystals would be no longer mixed crystals, but they would just possess the true characteristics of real chemical *compounds*; *the characteristic feature* for these, — contrary to what is the case for mixed crystals, — *is, that crystallographically-equivalent places of the space-group must be always occupied by identical atoms or atom-groups.* It was, indeed, experimentally shown, that in those cases, in which *new* diffraction-lines were observed in the ROENTGEN-spectograms, the occurrence of chemical compounds had already been proved before by means of thermic or electric methods. BAIN [1]), for instance, found such new lines in the series of mixed crystals of *gold* and *copper*, in the stoechiometric proportion: 1 : 3, — a fact, which he erroneously considered to be a corroboration of TAMMANN's theory of mixed crystals. BAIN's results were also stated by JOHANSSON and LINDE [2]), who found new lines in the proportion: 1 : 1 also. But the last mentioned investigators remark rightly, that just at the same concentrations, thermic analysis as well as electrical conductivity-measurements by KURNAKOW, ZEMCZUSNY and ZASEDATALEV [3]) have proved the existence of two chemical compounds between the two metals. Even after a long annealing of other mixtures of this series, if having simple stoechiometric proportions, JOHANSSON and LINDE could not prove the occurrence of new diffraction-lines in the ROENTGEN-spectrograms.

§ 6. The question has often been discussed, whether compounds and mixed crystals, if formed by the same components, must necessarily exclude each other, or not? Also in some cases it appeared to be very difficult to decide, whether a chemical compound or a mixed crystal were present in a special case.

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[1]) E. C. BAIN, Chem. and Metall. Engin., **26**, 655, (1922); **28**, 65, (1923).

[2]) C. H. JOHANSSON and J. C. LINDE, Ann. d. Physik, [4], **78**, 439, (1925).

[3]) N. KURNAKOW and *collaborators*, Journ. Inst. of Metals, **155**, 305, (1916).

The not numerous cases, in which these questions could be studied, are:

1⁰. The system: *calcite* ($CaCO_3$) — *dolomite* ($CaMg(CO_3)_2$) — *magnesite* (*giobertite* : $MgCO_3$). The external habit of these minerals is completely analogous [1]. By means of the method of specific weight-determination, RETGERS [2] was *not* able to decide, whether *dolomite* is a mixed crystal of the series or a compound. However, the complete proof, that *dolomite* is a chemical compound has been given by accurate crystallographical investigation, in connection with the ROENTGEN-analysis. *Calcite* and *magnesite* (*giobertite*) crystallise both in the *ditrigonal-scalenohedral* class. By means of the method of corrosion-figures it had already become probable, that the symmetry of *dolomite* is not higher than that of the *rhombohedral* class. Indeed, HAGA and JAEGER [3] by means of LAUE-radiograms, obtained by a pencil of ROENTGENrays incident perpendicularly to a crystal plate cut parallel to $\{0001\} = \{111\}$, could prove, that the three vertical symmetry-planes present in *calcite*, are *absent* in *dolomite*. The structure of *calcite* now, is such, that, if the planes of gliding symmetry in it be thought eliminated, by the presence of which the one half of the *Ca*-atoms can be brought to coïncidence with the other half, the crystallographically-equivalent places, originally occupied by *Ca*-atoms, will be simultaneously differentiated in two kinds of positions, which are no longer equivalent to each other. Thus at the same time the opportunity is created, to substitute both kinds of places by *Ca*- and *Mg*-atoms alternately; and this is exactly what happens in the "compound": $CaMg(CO_3)_2$. Indeed, ROENTGEN-analysis showed, that the crystalstructure of *dolomite* is in full agreement with this view [4].

2⁰. The second known case of this kind, refers to the system: *sodiumsulphate* (Na_2SO_4) — *glaserite* ($3\,K_2SO_4, Na_2SO_4$) — *potassiumsulphate*: (K_2SO_4). By determination of the specific weights, RETGERS [5] could corroborate the view, that *glaserite* is a "compound". Also in this case, only a slight deviation from the stoechiometric composition occurs, which is a consequence of a limited formation of mixed crystals.

3⁰. More extensive series of mixed crystals were observed in the system: $\{Al(C_2O_4)_3\}Na_3, 4^1/_2\,H_2O - \{Al(C_2O_4)_3\}(NH_4)_3, 3H_2O$ in which system at the same time a double salt: $\{Al(C_2O_4)_3\}_2Na_3(NH_4)_3, 7\,H_2O$ occurs. [6]

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[1] The composition of these minerals sometimes deviates a little from the stoechiometric proportion, as a consequence of a mixing of both components within narrow limits.

[2] J. W. RETGERS, Zeits. f. phys. Chem., **6**, 191, (1890).

[3] H. HAGA and F. M. JAEGER, Proceed. Kon. Acad. v. Wetensch. Amsterdam, **18**, 548, (1916); cf. Plate II.

[4] W. H. and W. L. BRAGG, *X-Rays and Crystal-Structure*, 3d Edit., (1918), 112.

[5] J. W. RETGERS, Zeits. f. phys. Chemie, **6**, 191, (1890).

[6] G. WYROUBOFF, Bull. Soc. fr. Minér., **23**, 65, (1900); W. STORTENBEKER, Rec. **32**, 226, (1913).

4⁰. In the systems: $SrCl_2—SrF_2$; $BaCl_2—BaF_2$; and $CaCl_2—CaF_2$ [1]), besides extensive mixing series, also the occurrence of compounds between the components in the proportion: 1 : 1 was proved by means of thermic analysis.

5⁰. Finally by the same method, the occurrence as well of continuous mixing series from 0 % till 100 %, as of intermediate compounds was established in the following systems:

a. $Br—I$; compound: BrI. [2])

b. $Mg—Cd$; compound: $MgCd$. [3])

c. $Au—Cu$; compounds: $AuCu_3$ and $AuCu$. [4])

As has already been said, the last mentioned system has been also investigated after the ROENTGENographic method by JOHANSSON and LINDE. The new diffraction-lines on the ROENTGENspectrograms were not only observed in such proportions of both components, as correspond with the composition of the compounds mentioned above; but they appeared on the films also, be it with slighter intensities, if the composition differed from these of the compounds themselves, until at last they disappeared completely. This behaviour is such, as might be expected according the theory of the statistical distribution of the isomorphously substituting atoms: the absence or presence of certain symmetry-elements manifests itself *gradually*, on approaching the composition of the compounds or on withdrawing from it. The transition from the one space-group to the other occurs evidently gradually.

§ 7. If now the system: $MgSO_4$, $7\,H_2O—ZnSO_4$, $7\,H_2O$ be considered more in detail in the light of what was said in the foregoing, we can remark that the occurrence of a continuous mixing series from 0 % till 100 % does not exclude the possibility of the eventual occurrence of "compounds" between the components within this series. It was proved in a convincing way, that in the case considered, the crystal-class remains always the same throughout the whole series. Not only was it impossible to state any deviation in the crystal form [5]) of the mixed crystals of different composition, but, — what is of high interest, — DUFET [6]) was able to prove that a complete *proportionality* exists between the composition of the mixed crystals and their middle refraction-coëfficient β; the same appeared to be true with respect to their specific weights.

As the pure sulphates crystallize in the class of the lowest symmetry of the rhombic system (bisphenoïdal), and as it may safely be assumed that compounds which are formed by partial substitution of one metal by the atoms of another, will surely have no higher symmetry than the pure components, — it appears evident that an eventually occuring compound, within the series considered, of *another* symmetry than that of the components, would only crystallize either in the monoclinic or in the triclinic system. A more or less appreciable alteration of the optical behaviour would undoubtedly be than observed at the same time.

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[1]) W. PLATO, Zeits. f. phys. Chem., **58**, 350, (1907).

[2]) P. C. E. MEERUM TERWOGT, Zeits. f. anorg. Chemie, **47**, 203, (1905).

[3]) G. GRUBE, Zeits. f. anorg. Chem., **49**, 72, (1905); G. URASOW, ibid. **73**, 31, (1912); G. BRUNI and C. SANDONINI, ibid. **78**, 277, (1912).

[4]) N. KURNAKOW and collaborators, Journ. Instit. of Metals, **155**, 305, (1916).

[5]) C. VIOLA, Zeits. f. Kryst., Festband P. GROTH, **58**, 583, (1923).

[6]) H. DUFET, Bull. Soc. fr. Minér., **12**, 22 (1889).

In the rhombic system a compound of the type: $Mg_2 Zn (SO_4)_3$, 21 H_2O is already higly improbable, because of the fact, that in the space-groups belonging to this system, only 1-, 2-, 4-, 8-, 16-, and 32-fold equivalent places can occur. A number of groups (SO_4), which is equal to 3 or to a multiple of 3, can find its place in an elementary cell of rhombic symmetry therefore only in positions, which are *not* equivalent to each other. In this particular case it can be proved, however, that a compound: $Mg_2 Zn (SO_4)_3$, 21 H_2O is completely impossible here.

For it has been proved already [1]), that the space-group of the pure crystallized components: $MgSO_4$, 7 H_2O and $ZnSO_4$, 7 H_2O can be no other than V_4, and that the elementary cell contains 4 molecules.

Of mixed crystals of different concentrations, rotation-spectrograms were made with successive rotation of the crystals round each of the crystallographic axes. From these it was seen, that the identity-distances of the mixed crystals did not differ appreciably from those in the same direction in the case of the pure components. Moreover, DUFET showed, that the specific weights varied practically proportionally to the concentration. In each case the elementary cell contains 4 molecules: $Mg (Zn) SO_4$, 7 H_2O. A molecule: $Mg_2 Zn (SO_4)_3$, 21 H_2O is, therefore, impossible in this series, because the specific weight of it should necessarily be much smaller than that found experimentally, if the cell only contained a single molecule of this composition, and much greater than the observed value, if the cell contained two molecules of it.

§ 8. By the study of these rotation-spectrograms and of such obtained after BRAGG's method, in the case of mixed crystals, whose compositions deviated only slightly from the proportions: $MgSO_4 : ZnSO_4 = 1 : 1$ and 2 : 1, — it was undeniably demonstrated, that the space-group in these cases always remains quite the same, i.e.: V_4.

From the dimensions of the grating and the specific weights observed, it becomes evident, that 2 molecules of a compound: $MgZn(SO_4)_2$, 14 H_2O would have to be placed into the elementary cell. But this cannot be done in any way so, that the *Mg*- and *Zn*-atoms shall come pairwise in equivalent positions, because the space-group V_4 has only *four*fold equivalent positions. From this the conclusion must, therefore, be drawn, that also this so-called "compound", indicated by HOLLMANN as such, can, by no means be a true compound. In this connection it is of interest to remember, that BECKENKAMP [1]) in his criticism of HOLLMANN's work, drew the conclusion, that the elementary cells of the heptahydrates of the rhombic sulphates of this kind must contains of 6 molecules or a multiple of 6, making the supposition, that the compounds indicated by this author really existed. In the case of the presence of 6 molecules $MgSO_4, 7\,H_2O$, then respectively 3×2 or 2×3 of these molecules must be thought to be substituted by 3 molecules of $MgZn(SO_4)_2, 14\,H_2O$ and 2 molecules of $Mg_2Zn(SO_4)_3, 21\,H_2O$. Reversely, in this paper, it has been proved, that the elementary cell contains 4 molecules $MgSO_4, 7\,H_2O$, and from this the conclusion has been drawn, that some errors must have been introduced into HOLLMANN's experiments or into his reasonings, the occurrence of these two compounds being, from the structure point of view, impossible.

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[1]) H. G. K. WESTENBRINK, these Proceed. 29, (1926), p. 1223.

Groningen, Laboratory for Inorganic and
Physical Chemistry of the University.

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1) J. BECKENKAMP, Zeits. f. Kryst., 37, 523, (1903).

Histology. — *"Concerning an Optic Phenomenon in Tendons and on double refraction Gratings."* By M. MINNAERT Sc.D. and Prof. G. C. HERINGA M.D. (Communicated by Prof. A. PANNEKOEK.)

(Communicated at the meeting of September 25, 1926).

When looking through a longitudinal section of a tendon at a source of light, placed at some distance, we shall observe a row of diffraction images resembling those viewed through a grating of which the grooves are *perpendicular* to the direction of the fibres of the tendon. Between crossed nicols the central image and the diffraction spectra of even number are extinguished; between parallel nicols the uneven numbered spectra disappear. Under the microscope the fibres exhibit a regular undulation, whose period (40 μ) corresponds with the one calculated from the diffraction angle. We have described the phenomenon in an earlier number of these Proceedings [1]. We now purpose to look more closely at the relation between the internal structure of the tissue and the optic diffraction phenomenon.

We start from the conception that the fibres constituting the tendon are to be considered as quasi-uniaxial crystals, their axis being directed like the fibres [2]. The microscopic picture goes to show that these crystal filaments are either undulating like *sine lines* in a plane, or winding in *helices*. A similar structure possesses all the properties of an optic grating, of which, however, the diffraction is caused by double refraction, for which reason we shall call it *double refraction grating*. We shall now try to ascertain what diffraction images must originate with sine lines and with helices.

1st hypothesis.

The fibres are disposed like sine lines in a plane.

Let the x-axis be in the longitudinal direction of the tendon and let the course of the fibres be expressed in the equation: $y = a \sin x$.

The angle which the fibres make with the x-axis then is: $\vartheta = \operatorname{arc\,tg} \dfrac{dy}{dx}$

so that

$$\sin \vartheta = \frac{a \cos x}{\sqrt{1 + a^2 \cos^2 x}} \quad , \quad \cos \vartheta = \frac{1}{\sqrt{1 + a^2 \cos^2 x}}.$$

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[1] Proc. Acad. Amst. 1926, **35**, 763.

[2] For our observations it does not matter whether this birefringency is really caused by micellar double refraction or by bacillar double refraction ("Stäbchen doppelbrechung)", or by a combination of the two.

This preparation is now illuminated by a parallel beam of polarized light, of which the vector may have the amplitude 1, and may travel along the x-axis (Fig. 1). When the rays pass through the crystal, the vibration is decomposed into OK and OG normal to OK. With crossed nicols both waves are recombined by the analyzer along OA. Their amplitude is now $\sin \vartheta \cos \vartheta$. In case the preparation be very thin they would destroy each other by interference. With a thicker preparation a difference of phase originates, inducing a wave $c \sin \vartheta \cos \vartheta$; the interference phenomena are strongest when c reaches its maximum value 2; after this they will decrease again.

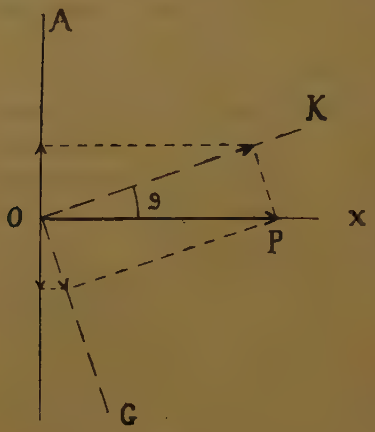

Fig. 1.

Likewise the transmitted vibration is with parallel nicols: $1-c\cos^2\vartheta$, c again reaching no higher than 2.

In these two cases, then, the transmitted amplitude is respectively

$$\frac{a c \cos x}{1+a^2\cos^2 x} \quad \text{en} \quad 1-\frac{c}{1+a^2\cos^2 x}$$

ergo a periodic function of the place along the tendon.

It appears, then, that our *double refraction grating* practically works as a sort of *absorption grating* of which the transparency fluctuates periodically. It is remarkable, though, that in the first case the average transmitted amplitude is *zero*; the consequence of this is that the central image is lacking, a phenomenon that can never occur with true absorption gratings, whatever may be the shape of their transmission curve.

Now, the general grating theory tells us that the transmitted amplitude which is a function of x must be analyzed into a series after FOURIER; let N be the coefficient of a definite term, then $\frac{N^2}{4}$ is the relative intensity of the light of the corresponding diffraction image relative to the incident beam.

In this way we find the following relative intensities, assuming a to be $= 0.5$ (consequently rather flat sine lines), and $c = 2$, which holds approximately for our thickest preparations.

	1st diffraction image	2nd diffraction image	3th diffraction image
Crossed nicols	0,178	0	0,0005
Parallel nicols	0	0,0100	0

We see thus that even this simple theory gives a very satisfactory explanation of the observed phenomena.

When rotating the analyzer the uneven-numbered diffraction maxima and the even-numbered maxima with the central image are extinguished alternately. When the analyzer is removed, the different spectra are seen simultaneously. The light intensities found seem to be of the right order of magnitude.

Finally it is also easy to see that the phenomena must be quite the same when we work without an analyzer and let the incident light vibrate not in the longitudinal direction of the tendon, but in any given direction; and our observation confirms this conclusion, so that we have also found an explanation for the image in natural light.

But the phenomena are somewhat less defined than is suggested by the theory. The central image and the spectra are never extinguished completely; the changes of intensity of the second diffraction image do not seem to be so considerable as could be expected. These differences will be readily understood if we reflect that the shape of the fibres is not that of a pure sine line.

2nd hypothesis.

The fibres are wound in helices.

When we are examining the preparation, the angle between our line of sight and the optic axis varies with the distance x along the tendon. We know that in a crystal the vibrations of the ordinary and of the extraordinary ray are parallel and perpendicular to the principal plane, and therefore they must be in each point of our preparation parallel and perpendicular to the projection of the optic axis (the direction of the fibres).

Now let us conceive a uniaxial crystal in the centre of a unit sphere with its optic axis directed along OA (fig. 2). We rotate the crystal round a mechanical axis OC, which makes with OA the angle ψ, while the observer keeps looking at the crystal from OB. A still simpler method is to conceive of the crystal as being in rest, but to let OW travel round the great circle normal to OC.

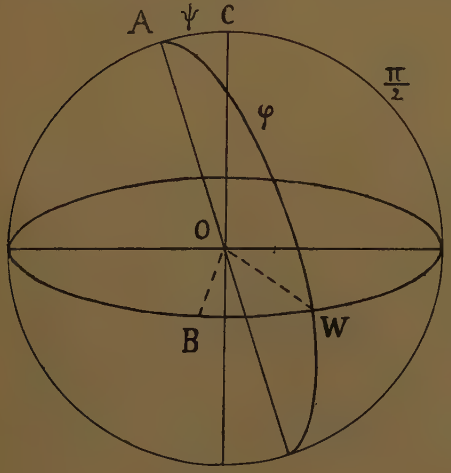

Fig. 2.

When counting all the azimuth angles from OB, where the axis OA is seen at its greatest elongations, the arc BOW is $= x$.

Therefore, between the direction of observation and the optic axis the angle $AOW = \varphi$ is given by:

$$\cos \varphi = \cos \left(\psi + \frac{\pi}{2} \right) \sin BOW = - \sin \psi \, . \, \sin x.$$

The velocities of propagation of the ordinary and the extraordinary wave in the crystal are:

$$V_\omega = a$$

$$V_\varepsilon = \sqrt{a^2 \cos^2 \varphi + c^2 \sin^2 \varphi} = c + \frac{a^2 - c^2}{2c} \sin^2 \psi \,.\, \sin^2 x$$

when the double refraction is not strong. The velocities a and c are then respectively the largest and the smallest that can occur in the crystal. During the passage of a thickness D of the crystal there originates between the ordinary and the extraordinary ray a difference of phase

$$\frac{2\pi D}{\lambda} (n_\varepsilon - n_\omega) (1 - \sin^2 \psi \,.\, \sin^2 x),$$

in which λ represents the wave-length in air.

Now in order to examine the action of such a preparation as a grating, we again make the direction of the vibration of the incident light parallel to the X-axis (OC in fig. 2), and we suppose the nicols to be crossed.

We have now to compound:

$$\frac{a \cos x}{1 + a^2 \cos^2 x} \sin 2\pi \frac{t}{T};$$

and

$$-\frac{a \cos x}{1 + a^2 \cos^2 x} \sin \left[2\pi \frac{t}{T} + \frac{2\pi D}{\lambda} (n_\varepsilon - n_\omega) (1 - \sin^2 \psi \,.\, \sin^2 x) \right].$$

For further calculations we again assume that the phase-difference for $x = 0$ has reached the value π. Then the resultant vibration is:

$$\frac{2a \cos x}{1 + a^2 \cos^2 x} \cos \left(\frac{\pi}{2} \sin^2 \psi \,.\, \sin^2 x \right) . \sin \left(2\pi \frac{t}{T} - \frac{\pi}{2} \sin^2 \psi \,.\, \sin^2 x \right).$$

Likewise we find with *parallel nicols:*

$$\left(1 - \frac{2a^2 \cos^2 x}{1 + a^2 \cos^2 x} + \frac{\pi^2}{2} \sin^4 \psi \,.\, a^2 \,.\, \frac{\cos^2 x \,.\, \sin^4 x}{1 - a^4 \cos^4 x} \right) .$$
$$\sin \left(2\pi \frac{t}{T} + \pi \sin^2 \psi \,.\, a^2 \frac{\sin^2 x \cos^2 x}{1 - a^2 \cos^2 x} \right).$$

So *this* double refraction grating *also* acts as an absorption grating. If we compare the amplitude with the one for the birefringent sine lines (p. 1386) we shall see that there is an additional small term. But besides this there is also a periodic change in the phase. This double refraction grating acts as an absorption grating and at the same time as a *retardation grating*. The calculation of the FOURIER-coefficients gives us, as before, the intensity of the light of the different diffraction images. The result of the somewhat tedious calculations is

	1st diffraction image	2d diffraction image
Crossed nicols	0.174	0
Parallel nicols	0	0.0094

A comparison with the corresponding table on p. 2 shows that the diffraction images must be always the same in the 1st and in the 2d hypothesis. The differences are so small as to elude measurement with our equipment. So the optic phenomenon can be explained on the hypothesis of the sine lines as well as on that of the helices; the latter hypothesis is supported only by what has been brought forward in our previous paper (p. 767).

(*From the Physical Laboratory and the Laboratory for Embryology and Histology of the State University at Utrecht*).

Utrecht, September 1926.

Physiology. — *„On the Isolation of the anti-beri-beri Vitamin."* By B. C. P. JANSEN and W. F. DONATH. (Communicated by Prof. C. EYKMAN.)

(Communicated at the meeting of September 25, 1926).

The first attempts to isolate the substance that, according to EYKMAN's 1) fundamental investigations, possess a prophylactic property against beriberi, were made by G. GRYNS 2), but they were ineffectual. EYKMAN 3) found still a number of properties of this substance, among which the very remarkable one that it is easily soluble in water and in 80° alcohol, and readily dialysable. This is of vital importance, as it goes to show that this substance has a comparatively small molecule, and on that account cannot be classed under the proteins, nucleoproteids, and the like. In view of its considerable physiological activity it probably belongs to the group that BARGER has included under the general name of the "simpler natural bases" and was termed by GUGGENHEIM "die biogenen Amine".

In 1911 C. FUNK 4) published his first study on this substance which he designated by the name of "vitamin". In this publication he described a body, 20—40 mgrms. of which could cure a pigeon that had developed polyneuritis after a diet of polished rice. It appeared later on that this was not the "vitamin" sought for. Furthermore the symptoms that occurred on a diet of purified proteins + fats + carbohydrates + salts warranted the assumption of several of such "vitamins", which were differentiated by the designations A and B, afterwards also C, D and E, etc. vitamins. It is still a moot point, which may now be expected to be soon set at rest, whether the B-vitamin, described by the American and English observers, which was noted for its influence on the growth of young rats, is identical with the anti-beriberi- or anti-neuritic-vitamin, that protects man against beriberi and birds from polyneuritis 5). This identity was discredited by authors as EYKMAN 6) and MENDEL 7). After FUNK a good many observers have tried

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1) C. EYKMAN, Geneesk. Tijdschr. voor Ned.-Indië, **36**, p. 214 (1896).

2) G. GRIJNS, Geneesk. Tijdschr. voor Ned.-Indië, **41**, p. 1 (1901).

3) C. EYKMAN, Arch. f. Hygiene, **58**, p. 150 (1906).

4) C. FUNK, Journ. physiology, **43**, p. 395 (1911).

5) See H. H. MITCHELL, Journ. biol. Chem., **40**, p. 399 (1919) and A. D. EMMETT and G. O. LUROS, Ibid. **43**, p. 265 (1920).

6) C. EYKMAN, C. J. C. VAN HOOGENHUIJZE and T. J. G. DERKS, Journ. biol. Chem. **50**, p. 311 (1921).

7) CROLL and L. B. MENDEL, Americ. Journ. Physiol. **74**, p. 675 (1925).

B. C. P. JANSEN and W. F. DONATH: "ISOLATION OF THE ANTI-BERIBERIVITAMIN".

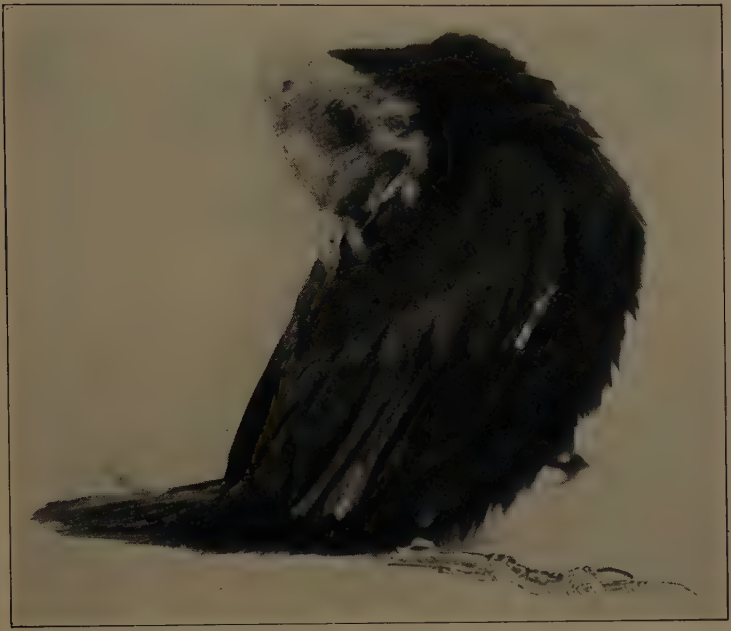

Fig. 1.
Ricebird (munia maja) with polyneuritis; about $1^1/_2 \times$ natural size.

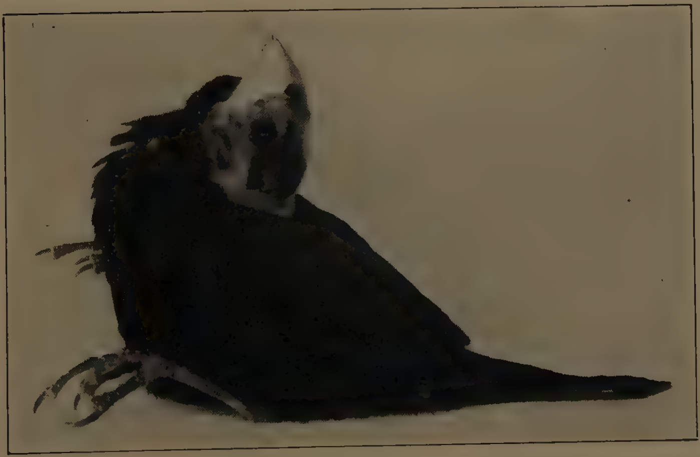

Fig. 2.
Ricebird (munia maja) with polyneuritis; about natural size.

to isolate the B-vitamin, and especially the anti-beriberi-vitamin, without any positive results, so far as we know. A review of their work can be found in the modern books on vitamins, see e.g. "The Vitamins" by H. C. SHERMAN, and L. L. SMITH, New York 1922 pp. 18—48. Last year two articles appeared in the "Chemisch Weekblad" by American authors [1]), which contained a short survey of the work on the isolation of the antineuritic, resp. B-vitamin. This prompted us to publish in the "Chemisch Weekblad" a paper on the state at that time of our attempts to isolate the antineuritic vitamin [2]). At the same time we could set our mind more deliberately to the investigations that had occupied us for more than nine years already in the intervals of other work. To our great satisfaction we can say that we have succeeded in isolating the anti-beriberi-vitamin in the same laboratory where EYKMAN and GRYNS have worked.

For our earlier work we refer to the above-named article in the "Chemisch Weekblad" and to the various Annual Reports of the "Geneeskundig Laboratorium" of Weltevreden. In this paper we intend to describe the method that led to our ultimate success in isolating the anti-beriberi-vitamin.

The material we started with were the fine rice-polishings (dedek) that can be procured in India at a very low price. An extract of it was fractionated in different ways. In order to determine the vitamin-content of the various fractions, we worked with small ricebirds called bondols (munia maja). Groups of ten of these birds, caged together, were fed with polished rice, to which was added a known quantity of the fraction under examination. The polished rice had previously been washed in running water for 2 × 24 hours, while the deficiency of mineral salts and A-vitamin was compensated by addition of 2 % of a salt-mixture, about equal to that used by OSBORNE and MENDEL, and of ¼ % codliver oil. These ricebirds are very fit reagents to testify the presence of the antineuritic vitamin, and to determine its content [3]). With a rare exception (no more than 1 or 2 % of the total number) all the ricebirds fed on washed, polished rice develop polyneuritis in from 9 to 13 days. (See Plate Fig. 1 and 2.) If 5 % of a definite sort of dedek is added to the rice, polyneuritis reveals itself only after from 15 to 23 days.

We now determined every time the quantity of the different that had to be added to the washed, polished rice, so that the 10 rice-birds fed with this mixture contracted polyneuritis within from 15 to 23 days. As we found that a ricebird ingests on an average 2 grms of rice a day, we could compute the quantity of a definite fraction per bird and per day that had to be added to the rice, to guard the animals from polyneuritis for 15—23 days.

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[1]) A. SEIDELL, Chem. Weekblad 22, p. 353 (1925) and P. A. LEVENE and B. VAN DER HOEVEN, Chem. Weekblad 22, p. 575 (1925).

[2]) B. C. P. JANSEN and W. F. DONATH, Chem. Weekblad 23, p. 201 (1926).

[3]) Vide B. C. P. JANSEN, Mededeelingen Geneeskundig Laboratorium te Weltevreden 1920, p. 40.

For some kinds of dedek a quantity of 100 mgrms per ricebird and per day sufficed; however, with most commercial sorts this quantity amounted to 140 mgrs. Finely ground rice-polishings (dedek) were now extracted with tap-water. (The Batavian tapwater countains only about 130 mgrs of dissolved salts per Litre), to which 3½ cc of sulphuric acid had been added per Litre, to obtain the precise acidity (p_H ultimately = ± 4.5), and 200 cc of spiritus fortior to neutralize the action of micro-organisms. It seemed to us that formol was a less favourable disinfectant. The extraction was performed in a row of 4 wooden casks of ± 40 Litres each in accordance with the principle of the counter-current. The bottom and the lid of each cask was provided with an opening resp. for the affluence and the effluence of the liquid. A little above the bottom a second loose bottom had been applied for the greater part consisting of copper-gauze. On this gauze rests a layer of mineral grit, and on top of this the dedek (16 kg per cask). Every day one of the casks was refreshed, and the other three were moved up, so that the fresh dedek came in contact with the liquid that has already extracted the dedek in the other three casks, and the most extracted dedek was extracted with the fresh water-alcohol-sulphuric acid mixture. In this way almost 100 kg of dedek could be extracted every week. This extract contained ± 20 kg of solid matter and approximately all the vitamin contained in the dedek. SEIDELL showed in 1916 that the vitamin is absorbed selectively by Lloyd's reagent, a kind of fuller's earth. After a prolonged enquiry we discovered in the "acid clay" put on the market by the BÜNING concern of Cheribon, a variety of fuller's earth that possessed the same absorbing properties with respect to the vitamin as Lloyd's reagent.

The extract from 100 kg of dedek was now diluted to 300 Litres (the p_H was if necessary raised to 4.5) and mixed with 300 kg of very finely ground acid clay. After some hours' stirring of this mixture by means of an electromotor, the acid clay was allowed to subside and the supernatant fluid was pipetted off. Finally the activated acid clay was sucked off in a filter of a surface of 45 × 60 cm acid, washed repreatedly with small amounts of water acidulated to p_H = 4—5, the residue was removed from the filter and treated with so much baryta that a paper, soaked with tropaeolin 0, is turned reddish brown, when immersed in the fluid; the p_H then amounts to ± 12 or 13. This baryta-extract, which contains the vitamin, was again sucked off on the filter and then washed, first with baryta, subsequently with distilled water; to the filtrate sulphuric acid was added to an amount that made the acid red on congopaper. That treatment with baryta should pass off as rapidly as possible, because the vitamin is being deteriorated in alkaline solution. However, the solution, acidulated with sulphuric acid, may safely be left to stand for one or two days, after which the barium-sulphate will have subsided. Most of the supernatant fluid was then decanted off, and the remaining fluid was filtered off on a hardened paper filter. This filtrate still contains ± 100 grms of solid matter, and 80 % of the original vitamin present in the dedek. Now the acid clay-extract was again fractionated after KOSSEL and KUTSCHER [1]) with silver sulphate and baryta; their method was, however, refined by determining the p_H of the liquid. To this end the acid-clay-extract obtained from 100 kg of dedek was evaporated in a large porcelain dish placed in a heated water-bath. A very strong current of air was blown over the liquid by means of an exhauster, so that at a temperature of from 30° to 40° C. about 1½ to 2 Litres of water was evaporated per hour. The liquid was evaporated to a volume of ± 4 Litres. This was transmitted to a thick walled glass beaker of Pyrexglass of ± 10 Litres, and was subsequently treated with silversulphate or with silvernitrate. In our first experiments we used silver-sulphate partly in solution, partly as a solid. However, as it took some days of incessant stirring with an electromotor to dissolve a sufficient quantity of silversulphate, we used silvernitrate later on. Most often a quantity of ± 50 grms of silvernitrate was required. As known, the sufficiency of the addition will be attained when a sample of the liquid gives a brown precipitate directly on the addition of an excess of baryta. The addition of the silvernitrate to the acidulated acid-clay-extract yields a thick precipitate, not containing any vitamin. By violent stirring with an electromotor baryta was now allowed to flow in slowly from a burette or pipette. Then the p_H of the liquid (at the beginning only 2 or 3) rises slowly. The p_H was mostly determined with the aid of the capillator procured by the British Drug House, which gave us great satisfaction.

We are now able to supply so much baryta that the p_H rises to ± 4.5. In the resulting precipitate there is no appreciable quantity of vitamin. Now the liquid was filtered off and an amount of baryta was allowed to flow into it until the p_H became ± 6.5. In this second silverfraction there is rather more than 50 % of the vitamin contained in the acid-clay-extract. After filtering this deposit baryta is again added to the filtrate, until the $p_H = \pm 8.0$. In this 3rd silverfraction there is still a considerable amount of vitamin, but it is mixed with a relatively much larger quantity of inactive substances than in the 2nd silverfraction. Therefore, this 3rd silverfraction was not worked up directly, but the 3rd fraction of different preparations together, was again fractionated with silvernitrate and baryta after analysis with hydrochloric acid. In the filtrate of the 3rd silverfraction there is still a large amount of solid matter but practically no vitamin.

The 2nd silverfraction was decomposed with an excess of hydrochlorid acid, and filtered off from the consequent silverchlorid. This filtrate still included ± 20 grms of solid matter. The quantity required daily for a rice-bird, amounts to ± 0.080 mgrm = 80 γ. In a testing sample of the filtrate the excess of hydrochloric acid was determined by titration with alkali and an amount of sulphuric acid was then still added to raise the total acid-concentration, computed on sulphuric acid, to 5 %. Now a solution of phosphotungstic acid in 5 % sulphuric acid was added until a new addition no longer yielded a precipitate. The phosphotungstic acid was first purified after WINTERSTEIN[1]), by shaking up the aqueous solution with sulphuric acid and ether, the phosphotungstic acid passing into the latter fluid. This treatment with phosphotungstic acid may also precede the fractionation with silver and baryta, with the same favourable result. Then, however, much more phosphotungstic acid is required, and our store of this acid was limited, whereas silver nitrate could be procured in sufficient quantity. When the fractionation with silver + baryta is carried out before the treatment with phosphotungstic acid, no more than ± 40 grms of the latter is wanted per 100 kg of dedek. The phosphotungstic acid-precipitate was left to subside during 34 hours; it was subsequently filtered off on a suction-filter, and washed with 5 % sulphuric acid. Then the residue was sucked off completely and after this, for further purification, it was dissolved in acetone + water. This acetone-solution was, if need be, filtered and then poured into a large excess of 5 % sulphuric acid. Most of the phosphotungstic acid will then precipitate. A portion of it, however, remains in solution, but this no longer contains any vitamin worth mentioning.

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[1]) A. KOSSEL and P. KUTSCHER, Zeitschr. f. physiol. Chem. 31, p. 165 (1900).

After filtration this new precipitate of the phosphotungstic acid was decomposed with baryta. Once we tried to decompose it with ether and hydrochlorid acid after WINTERSTEIN, but we were not more successful, while the procedure was much more time-consuming.

When we decomposed with baryta, the precipitate was first dissolved again in acetone + water, concentrated baryta being added until, also after prolonged stirring, phenolphthalein-paper turned deep red. Rapid filtration of the barium-phosphotungstic acid precipitate followed, and a quantity of sulphuric acid was added to the filtrate, enough to throw down all the excess of baryta. A fortuitous surplus of the added sulphuric acid was removed with barium chlorid. Lastly the liquid was acidulated with hydrochloric acid. The solution still contains ± 5 grms of dry residue, while per ricebird and per day ± 30 γ is required to guard animals from polyneuritis for from 15 to 23 days.

It appears then that with this treatment with phosphotungstic acid no considerable purification is attained, but neither has a large loss of vitamin been caused, while substances have been removed, that are not eliminated in the succeeding procedure. This hydrochlorid solution was now evaporated to dryness, first on the waterbath, subsequently in vacuo over quick lime.

The sticky residue was now taken up in absolute alcohol, by which it was almost completely dissolved. A small quantity of insoluble material was filtered off and to the filtrate was added an alcoholic solution of platinic-chlorid. This yields a thick deposit of an orange tint. Virtually this deposit contains all the vitamin and only about ¼ of the solid matter present in the original alcoholic solution.

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[1]) E. WINTERSTEIN, Chemiker Zeitung, 1898, p. 539.

After 24 hours the platinum precipitate was filtered off, washed with absolute alcohol, taken up in water and decomposed with hydrogen-sulphid. Also after an excess of hydrogen sulphid is passed through the liquid one has to wait at the very least another 24 hours, before all the platinum-sulphid is thrown down. The filtrate of platinum-sulphid was evaporated first on the waterbath, then in vacuo over lime, a considerable portion of the dry residue resulting from it, is crystalline. Of the original quantity of solid matter in 100 kg. of dedek only about 1.4 gramme is left. The vitamin-content of the dedek used, was such as to necessitate the addition of ± 7 % dedek to the washed polished rice to protect the rice-birds against polyneuritis for from 15 to 30 days. It follows then that for 2 grms of rice i.e. the quantity ingested daily by a ricebird, 140 mgrms is required. So in 100 kg of dedek there is enough for about 700.000 ricebirds per day.

Of the platinum-precipitate analyzed with hydrogen sulphid ± 8 γ is required for a rice-bird. So in the 1.4 gr. there is enough for ± 175.000 ricebirds. It will be seen then that after all the above operations as much as ± ¼ is left of the vitamin contained in the dedek.

Although it took us long before we got so far, the knowledge obtained facilitates further experimentation. The substance thus isolated, is comparatively pure, as we shall see lower down that of the pure vitamin ± 3 γ per ricebird is wanted daily to guard these animals from polyneuritis for from 15 to 23 days. As about 8 γ of the decomposed platinum-precipitate is required per bird daily, this precipitate appears to consist for ± ¼ of the vitamin we are trying to isolate. However, further purification takes up a good deal of time and great loss results from it, as besides vitamin at least two more substances are to be found in this decomposed platinum-precipitate. This is evidenced by what follows: When we evaporate the solution that is obtained by treating the platinum-precipitate with hydrogen-sulphid after filtering off the PtS_2, subsequently evaporate it to dryness over quick lime, and finally dissolve the residue in absolute alcohol, part of it remains undissolved. The animal experiment shows that it is not the vitamin we are in quest of.

Treatment of the alcoholic solution with acetone produces a milky cloudiness from which after one or two days a partly viscous, partly crystalline deposit is set free against the bottom and the wall of the cask. Now this deposit is much richer in vitamin than the solution which, however, contains still a great part of the solid matter. So in the platinum precipitate we find anyhow: 1^0. a substance insoluble in absolute alcohol; 2^0. a substance that dissolves in absolute alcohol but is insoluble in acetone (this appeared to be the vitamin) and 3^0. a substance soluble in alcohol as well as in acetone. When we dissolve the precipitate with acetone in alcohol, part of it again remains undissolved: this then, is the substance insoluble in alcohol, which at the first treatment with alcohol remained in solution, in consequence of the presence of a large quantity of substances soluble in alcohol. We are now in a position to crystallize fractionally by dissolving as much of the decomposed platinum-salt as passes into solution in absolute alcohol. To this a little acetone is added, some of the precipitate adhering to the wall of the flask is decanted off and once more acetone is added to the liquid. Another precipitate appears and again some of it is decanted off, etc. Each of the precipitates is dissolved in absolute alcohol, which has been filtered off from the undissolved portion, and precipitated every time with renewed quantities of acetone, etc. By repeating this process several times we get at length the pure vitamin in the form of hydrochloric acid salt. However, after addition of the acetone it generally takes 24 hours, sometimes many days, before the initial milky cloudiness has completely subsided, so that the whole procedure takes months and months. When the vitamin is approximately pure, the operation progresses better, because during the treatment of the alcoholic solution with acetone a crystalline precipitate ensues directly, which does not cling to the wall.

We have endeavoured to correct this lengthy and sparingly productive process, but to little purpose so far. Picrolonic-acid gives a yellow-coloured precipitate, consisting especially of picrolonates of the vitamin, and of the substance insoluble in alcohol, the latter being most difficult of solution in water. Through recrystallization from diluted alcohol here also a separation can be attained, but not in a much easier way than through the alcohol-acetone fractionation, described above. With this picrolonic-acid fractionation the fractions can be recognized by their melting-point. The optimum-temperature of the picrolonate of the constituent insoluble in alcohol is 340° C.; that of the picrolonate of the vitamin is 165° (uncorrected).

The several picrolonic-acid-fractions (mostly no more than some tens of milligrammes) were filtered off to advantage in Gooch's mugs with porous bottom of sintered glass, from which the precipitate can be scraped off almost quantitatively with a platinum spatula without causing any pollutions through paper fibres.

By treatment with ether or ethylacetate and hydrochloric acid it is easy to separate the hydrochlorid from the picrolonate. Via the picrolonic-acid as well as with fractionation with alcohol and acetone we have ultimately obtained from 300 kg of dedek ± 100 mgrm of a crystalline substance, which also after recrystallization had a melting point of 250° C., as determined with the Anschütz thermometer: the so-called corrected melting-point. Already at rather more than 200° C. the substance begins to turn brown, but then melts rather sharply at 250° C. A portion of this substance was transferred by means of gold-chlorid to a beautifully crystallizing double-salt.

Now for the evidence that these crystals are, indeed, the antiberiberi vitamin hydrochlorid.

Of some hundreds of groups of 10 ricebirds each, fed on a mixture of washed, polished rice and inactive fractions, there was not one group of which all the birds or even most of them kept healthy for more than 12 days, while only very few individuals could hold out longer than 14 days. We now conducted the following experiments with the vitamin-hydrochlorid, besides a number of preliminary tests (all of which gave the same result as the experiments proper): Every time ten ricebirds were fed during ± 3 weeks with washed polished rice, to which different quantities of the vitamin-hydrochlorid had been added.

A. with vitamin purified through crystallization from absolute alcohol and acetone:

Cage I: 1 part vitamin-hydrochlorid to 1 million parts washed, polished rice; since the average daily diet of a ricebird is two grms of rice, this comes to 2 γ per bird and per day. One of the ricebirds contracts polyneuritis after 18 days, two after 23 days, the others are still in good health after 23 days.

Cage II: 1½ parts vitamin-hydrochlorid to 1 million parts washed, polished rice, i.e. 3 γ per bird and per day. After 3 weeks all the animals are healthy.

B. with vitamin-hydrochlorid purified via picrolonic acid:

Cage III: 1 part vitamin-hydrochlorid to 1 million parts washed polished rice; i.e. 2 γ per bird and per day; three ricebirds polyneuritis after resp. 13, 18 and 20 days. The others still healthy after 3 weeks.

Cage IV: 1½ parts vitamin-hydrochlorid to one million parts washed, polished rice; i.e. 3 γ per ricebird and per day. After 3 weeks all are healthy.

C. with vitamin-hydrochlorid obtained through decomposition of the double salt with hydrogen-sulphid:

Cage V: 1 part vitamin-hydrochlorid to 1 million parts washed polished rice; i.e. 2 γ per ricebird and per day. This experiment has been in progress for 14 days now, but all the animals still keep in good health.

Cage VI: 2 parts vitamin-hydrochlorid to 1 million parts washed, polished rice; i.e. 4 γ per ricebird and per day. After 3 weeks all the animals are quite well.

The foregoing justifies us in assuming 2 γ per ricebird and per day to be the critical limit; of the 30 ricebirds, fed with it, only one develops polyneuritis inside of 15 days; the majority keep in good health even for more than 3 weeks. Of the ricebirds that received 3 γ or 4 γ hydrochlorid daily not one developed polyneuritis.

We have repeated these experiments with pigeons:

A. with hydrochlorid purified via the picrolonate.

Pigeon 1 and 2: 1 part vitamin-hydrochlorid to 400.000 parts washed, polished rice. For a pigeon that ingests ± 12 grms a day, this comes to 30 γ a day. After 5 weeks the foodstuff was finished; the pigeons looked quite well, but their bodyweight was reduced resp. from 267 to 222 and from 270 to 235 gms.

Pigeon 3 and 4: 1 part vitamin-hydrochlorid to 200.000 parts washed, polished rice; i.e. 60 γ per pigeon per day. After 6 weeks the food was finished; the pigeons still looked quite well; the weight of the one pigeon had remained quite the same, that of the other had been slightly lowered, viz. from 270 to 213 gms.

In these pigeon-experiments the ratio of vitamin to rice was taken somewhat liberally, as we do not know beforehand whether ricebirds and pigeons require a relatively equal quantity of vitamin per day. However, the results being so favourable, we afterwards took he same ratio for both birds in the preparation purified by absolute alcohol and acetone.

Pigeon 5 and 6: 1 part vitamin-hydrochlorid purified with alcohol and acetone, to 1 million parts washed, polished rice, i.e. ± 12 γ per pigeon and per day. The test is proceeding for 4 weeks only, but the animals look well, only the weight is lessened a little, viz. from 271 to 245 grms, and from 292 to 235 grms.

Pigeon 7 and 8: 2 parts vitamin-hydrochlorid purified with alcohol and acetone to 1 million parts washed polished rice, i.e. ± 24 γ per pigeon and per day. This test is also in progress only 4 weeks, but the animals look thriving while their weight is hardly lessened, viz. from 322 to 314 grms and from 302 to 291 grms. Since ± 1 % proteins is lost in the twice 24 hours' washing of the polished rice, so that the protein-content of the washed rice amounted to only 5.5 %, it is not impossible that a deficiency in protein was responsible for the decrease in the weight of some animals. For this reason we added in the last two experiments 3½ % thoroughly minced meat, extracted repeatedly with boiling water, which meat, as appeared from advisedly arranged experiments, contained no appreciable quantity of antineuritic vitamin.

Now if we consider that the pigeons fed only on washed, polished rice develop polyneuritis most often within 2 or 3 weeks, mostly with a marked loss in bodyweight if not forcibly fed, the great influence of the slight addition of the vitamin-hydrochlorid becomes very evident. To make assurance double sure, we also administered to two pigeons the same washed polished rice, to which, as with the last pigeons, had been added 2 % salts + 2½ % extracted minced meat, but no vitamin chlorid. The one developed polyneuritis after 24 days, the other after 25 days, while their weight decreased resp. from 312 to 207 gms and from 289 also to 207 gms.

The pigeons to which an admixture of vitamin-hydrochlorid was administered, also behaved differently from those that had washed polished-rice alone. The latter practically cease eating spontaneously already after a few days, while it looks as if they are rummaging for the few grains to which a trace of silverlayer still adheres, and throw away the other grains, thus making a mess of their diet; the former, including the pigeons on only 1 part vitamin-hydrochlorid to 1 million parts washed polished-rice, finish their allowance with great relish.

From these experiments, therefore, we may safely conclude that the hydrochlorid, detected by us, with a melting point at 250° C., is in a high degree instrumental in warding off polyneuritis. But the question may be asked whether this salt is indeed the vitamin-hydrochlorid, or whether perhaps the salt is contaminated with a small quantity of a still more active component that may be the vitamin that we endeavour to isolate. We believe that the latter supposition is altogether erroneous, if we consider that the salt has been purified through recrystallization, while the mother-lye appeared to be much less active. If the supposition were right, we should have to assume that the crystals had absorbed by selection the active component from the liquid, and had detained it after recrystallization, and transference to goldsalt and back again to hydrochlorid. To be sure this idea must really be precluded.

So a proportion of 1 or 2 parts vitamin to 1.000.000 parts rice would accordingly create in a man, who consumes ± 500 gms of rice a day, a want of ½ or 1 mgrm of vitamin. This is of the same order of magnitude as what we know of the consumption of other substances with great physiological activity, such as thyroxin, adrenalin, and the like.

Until it is quite purified the vitamin-hydrochlorid crystallizes in bundles of needles. The pure salt consists of rosettes of bundled rodlets. The hydrochlorid in a pure state is not hygroscopic ; but it is readily soluble in very little water ; it is also soluble in ethyl-, and methyl-alcohol, the solution in ethyl-alcohol gives a precipitate with an admixture of amyl-alcohol, acetone, ether, chloroform, benzol, petroleum-ether or ethyl-acetate.

A 2 %-solution of the hydrochlorid in water produces the following reactions : Sublimate yields a slight precipitate that becomes stronger by adding sodium-acetate ; from a solution of mercuric-sulphate in dilute sulphuric acid a thick precipitate ensues ; with iodin potassium-iodid a fine black precipitate originates ; with picric acid a cloudiness arises ; styphninic-acid yields a precipitate ; Dragendorff's reagent, a solution of bismuth-iodid in potassium-iodid solution, gives a thick, reddish precipitate; with zinc-chlorid, cadmium-chlorid, lead-acetate, copper-acetate, potassium-chromate, potassium-salphocyanate, and with perchloric acid, no precipitate comes forward. As is evident from the preparation, phosphotungstic acid, picrolonic acid and gold chlorid give a precipitate, the last two consisting of needle-shaped crystals. The aqueous solution does not give a precipitate with platinic-chlorid, the solution in absolute alcohol with an alcoholic solution of platinum-chlorid, does. By treating with sulphanilic acid and nitric-acid, and subsequently with soda, we observe an intensely red colour (diazo-reaction of Pauly).

In the hydrochlorid no other elements appeared to occur than C, N, H, O and Cl. After transference of the hydrochlorid to the nitrate we could demonstrate that no halogens occur in the vitamin itself.

Of the hydrochlorid and of the gold-double salt we made some elementary-analyses by means of PREGL—MÜLLER—WILLENBERG's micro-apparatus with quartz-tube and ground-in absorption tubes. We publish these results only provisionally. Within a few months we hope to be able to repeat these analyses with larger quantities of material.

We found :

Of the gold-salt :

13.775 mgrms give 2.864 mgrms H_2O, 7.447 mgrms CO_2 and 5.852 mgrms Au;
found : 2.31 % H, 14.74 % C. and 42.48 % Au.

Duplicate : 14.876 mgms give 3.505 mgms H_2O, 8.072 mgms CO_2 and 6.278 mgms Au;
found : 2.07 % H, 14.80 % C. and 42.20 % Au.

10.589 mgms gives with micro-Kjeldahl 0.461 cc^3 $\frac{n}{10}$ NH_3;
found : 6.1 % N.

8.991 mgms give 0.50 cc (measured over water) N of 760 mm and 32° C.; found 6.08 % N 7.293 mgms give 8.901 mgms AgCl,
found : 30.21 % Cl.

Computed for $C_6H_{10}ON_2 . HCl . AuCl_3$:
2.36 % H, 15.45 % C, 42.48 % Au, 6.02 % N and 30.54 % Cl.

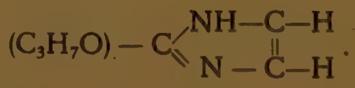
Of the hydrochlorid :

7.198 mgms give 4.515 mgms H_2O; carbon was lost;
found : 6.97 % H.

3.289 mgms give 2.894 mgms AgCl;
found : 21.77 % Cl.

Computed for $C_6H_{10}ON_2 . HCl$:
6.77 % H, 21.84 % Cl.

We see, then, that analyses correspond (not very beautifully though) to the formula $C_6H_{10}ON_2 . HCl$ for the hydrochlorid. Now, if we consider that fractionation with silver and baryta causes the body to precipitate in the histidingroup, whereas it gives a very intense red-coloration with the diazo-reaction of PAULY [1]), the suggestion is obvious that possibly there may be an imidazol-nucleus in the body, that also occurs in other substances essential to life, such as histidin, histamin and carnosin. The formula may then be imagined to be :



$$(C_3H_7O)-C\begin{array}{l}\nearrow NH-C-H\\ \qquad\qquad \| \\ \searrow N-C-H\end{array}.$$

But this has to be substantiated by later inquiry.

In conclusion we would take this opportunity of tendering our thanks to our analysts, especially to Raden SOEDARSONO, for their valuable assistance in the experimental work.

Weltevreden (Batavia), Medical Laboratory.
August 1926.

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[1]) H. PAULY. Zeitschr. f. Physiol. Chemie, **42**, p. 508 (1904); **44**, p. 159 (1905); **44**, p. 284 (1915).

Mathematics. — *"A property of 2-dimensional Elements"* by M. H. A. NEWMAN. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of October 30, 1926).

In a paper recently published in these Proceedings [1]) it was stated without proof that if $n > 2$ not every n-element can be transformed into an n-simplex by moves of type 2 alone, *i.e.* in certain n-elements there is no unit (n-simplex) whose removal leaves an n-element. It is the purpose of this note to prove this assertion by the production of an example (§ 2), and also to shew (§ 1) that if E_2 and S_2 are respectively a 2-element and a 2-simplex, then $E_2 \underset{2}{\rightarrow} S_2$.

A proof of the 2-dimensional JORDAN's Theorem, (in the combinatory sense), is included.

§ 1.

LEMMA. *If* E_2 *is a 2-element and* $\alpha\beta$ *an internal edge* [2]) *whose extremities belong to* $\overline{E_2}$ *and divide it into the parts* E_1' *and* E_1'', *then* E_2 *is the sum of two 2-elements with no common units, whose boundaries are* $\alpha\beta + E_1'$ *and* $\alpha\beta + E_1''$.

THEOREM 1. *If the 2-element* E_2 *is neither a simplex nor a complete star it has two detachable* [3]) *units with no common internal vertex.*

THEOREM 2. *If* $O_{12}(E_2) = q$, [4]) *and* S_2 *is a detachable unit of* E_2, *then* $O_{12}(E_2 - S_2) = q - 1$.

It is convenient to prove the lemma and the two theorems together. Let them be assumed true of elements of order less than q, (1, 2); and suppose that $O_{12}(E_2) = q$ in all three cases.

Proof of the Lemma. From the inductive hypothesis about Theorem 2 it follows that $E_2 \underset{2}{\rightarrow} S_2$. For if E_2 were derived from $\overset{*}{E}_2$, of order $q-1$, by the *removal* of a unit, $O_{12}(E_2)$ would be $q-2$, not q. Suppose then that T_2 is such that $O_{12}(E_2 - T_2) = q - 1$.

If T_2 contains $\alpha\beta$, (whose extremities lie in $\overline{E}_2$), the contact of T_2 with the rest of E_2 can only be regular if its remaining vertex is free; and then the required 2-elements are T_2 and $E_2 - T_2$.

If T_2 does not contain $\alpha\beta$, the part of $\overline{T}_2$ in $\overline{E_2 - T_2}$ belongs to one of the parts E_1' or E_1''. For if it had an edge in each they would necessarily be the pair of edges of $\overline{E_2 - T_2}$ at α, or the pair at β; and since the contact of T_2 is regular this is contrary to the supposition that α and β are in the boundary of E_2. Suppose then that the part $V.\overline{U}.$ of $\overline{T_2}$ belongs to E_1'. $\alpha\beta$ is interior to $E_2 - T_2$ and has its extremities on the boundary, and therefore divides it into two elements, E_2'' and E_2''', with boundaries $E_1'' + \alpha\beta$ and $(E_1' - V.\overline{U} + U.\overline{V}) + \alpha\beta$ respectively. Hence E_2 is divided by $\alpha\beta$ into the elements E_2'' and $E_2''' + T_2$, with boundaries $E_1'' + \alpha\beta$ and $E_1' + \alpha\beta$.

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[1]) M. H. A. NEWMAN, Proc. Roy. Ac. Amsterdam, 29 (1926) pp. 611 and 627, two parts here called FI and FII. The definitions of regular contact, moves of types 1, 2 and 3, *etc.*, are given in FI.

[2]) An *edge* is a 1-component.

[3]) A unit, S_n, of Γ_n, is *detachable* if it has regular contact with $\Gamma_n - S_n$.

[4]) "$O_{rs}(E) = q$", or "E is of order q, (r, s)", means that q is the smallest number of moves of types r and s by which E can be transformed into a simplex.

Proof of Theorem 1. Suppose, as before, that T_2 is a unit of E_2 such that $O_{12}(E_2 - T_2) = q - 1$, (and therefore $O_2(E_2 - T_2) = q - 1$). Let T_2 be $\alpha\beta\gamma$.

If $\alpha\beta$ is internal and γ free, $E_2 - \alpha\beta\gamma$, being of order $q-1$, contains two detachable units, of which at least one does not contain $\alpha\beta$. This simplex and $\alpha\beta\gamma$ are detachable units of E_2; and $\alpha\beta\gamma$ has no internal vertex.

If γ is internal and $\alpha\beta$ free, let $\xi\eta$ be a boundary edge of E_2 such that the unit $\xi\eta\zeta$ containing it does not contain γ. (There is such an edge, since E_2 is not a complete star). If ζ is interior to E_2, $\xi\eta\zeta$ is a second detachable unit, not containing γ. If ζ is in $\overline{E_2}$, $\xi\zeta$ divides E_2 into two 2-elements, both of order less than q (since $E_2 \underset{2}{\rightarrow} S_2$), of which one, say E_2', does not contain γ. E_2' has two detachable units, of which one at least does not contain $\xi\zeta$, and is therefore detachable from E_2. This is a second detachable unit, not containing the internal vertex, γ, of $\alpha\beta\gamma$.

Proof of Theorem 2. If E_2 is a complete star the theorem is obviously true. We suppose then that it is not a complete star.

Let T_2 be as before, and let $\varrho\sigma\tau$ be the given detachable unit S_2.

If $\varrho\sigma\tau$ has a free vertex, τ, the connected array $E_2 - T_2$, which contains $\varrho\sigma\tau$, must have $\varrho\sigma$ as an internal edge, save in the trivial case where $E_2 - T_2$ is $\varrho\sigma\tau$. Hence $E_2 - T_2 \underset{2}{\rightarrow} E_2 - T_2 - \varrho\sigma\tau$, which is therefore of order $q-2$; and $(E_2 - T_2 - \varrho\sigma\tau) + T_2$, which is $E_2 - \varrho\sigma\tau$, is of order $q-1$.

If τ is internal and $\varrho\sigma$ free, and T_2 does not contain τ, a similar argument shows that $O_2(E_2 - \varrho\sigma\tau) = q - 1$. If τ belongs to T_2, let U_2 be a detachable unit of E_2 not containing τ. U_2 is then detachable from $E_2 - T_2$; $(E_2 - T_2) - U_2$ is of order $q-2$, and therefore $O_2(E_2 - U_2) = q - 1$. The unit $\varrho\sigma\tau$ is detachable from $E_2 - U_2$, and therefore

$$O_2(E_2 - U_2 - \varrho\sigma\tau) = q - 2, \text{ whence } O_2(E_2 - \varrho\sigma\tau) = q - 1.$$

JORDAN's Theorem in two dimensions, of which the lemma is a special case, is now easily proved in its unrestricted form.

Theorem 3a. *If e_1 is a 1-element consisting of internal edges of E_2 but having its extremities, α and β, in $\overline{E_2}$, then E_2 is the sum of two 2-elements with no common unit, whose boundaries are $e_1 + E_1'$ and $e_1 + E_1''$, where E_1' and E_1'' are the parts into which $\overline{E_2}$ is divided by α and β.*

Suppose the theorem true of 2-elements of order less than q, and let $O_2(E_2) = q$. Let T_2 be such that $O_2(E_2 - T_2) = q - 1$. Clearly the part, (say $U.\overline{V}$), of $\overline{T_2}$ in $\overline{E_2}$ belongs either to E_1' or to E_1'' — say to E_1'.

If T_2 contains no internal vertex of e_1, $E_2 - T_2$ is divided by e_1 into two 2-elements, with boundaries $E_1' - U.\overline{V} + V.\overline{U} + e_1$ and $E_1'' + e_1$; and on adding T_2 to the first, the division of E_2 by e_1 is established.

T_2 cannot contain two edges of E_1 save in the trivial case where $V.\overline{U}$ is e_1. If it contains the edge $\alpha\xi$ and no other, $e_1 - \alpha\xi$ is interior to $E_2 - T_2$, and the proof is completed as before.

If T_2 contains an interior vertex, ξ, but no edge, of e_1, let $\overset{1}{e_1}$ and $\overset{2}{e_1}$ be the parts, (containing α and β respectively), into which ξ divides e_1, and $\overset{1}{\varepsilon_1}$ and $\overset{2}{\varepsilon_1}$ the corresponding parts into which it divides $E_1' - U.\overline{V} + V.\overline{U}$.

The 1-element $\overset{1}{e_1}$ is interior to $E_2 - T_2$, save for its extremities, and so divides it into, say, $\overset{1}{E_2}$ and $\overset{3}{E_2}$ with boundaries $\overset{1}{e_1} + \overset{1}{\varepsilon_1}$ and $\overset{1}{e_1} + \overset{2}{\varepsilon_1} + E_1''$. $\overset{2}{e_1}$ is interior to $\overset{3}{E_2}$, save for its extremities, and divides it into, say, $\overset{2}{E_2}$ and E_2'', with boundaries $\overset{2}{e_1} + \overset{2}{\varepsilon_1}$ and $\overset{2}{e_1} + \overset{1}{e_1} + E_1''$. T_2 has regular contact with $\overset{1}{E_2}$, and the 2-elements $\overset{2}{E_2}$ and $\overset{1}{E_2} + T_2$ have a single boundary edge in common. Their sum, E_2', is a 2-element, (F II Theorem 8*a*), whose boundary is $E_1' + e_1$. The two elements E_2' and E_2'' are the parts into which E_2 is divided by e_1.

Theorem 3*b*. *If Σ_1 is a circle contained in a 2-sphere, Σ_2, Σ_2 is the sum of two 2-elements, without common units, of both of which Σ_1 is the boundary.*

Let a unit, S_2, of Σ_2 containing an edge, $\alpha\beta$, of Σ_1 be replaced by $\xi.\overline{S_2}$, where ξ is a new vertex, (move of type 3). Theorem 3*b* is easily proved by applying, Theorem 3*a* to $\Sigma_2 - \xi\alpha\beta$, then replacing $\xi\alpha\beta$, and finally reversing the move of type 3.

§ 2.

Consider the 3-array, Γ_3, with the vertices

$$\alpha,\ \beta,\ \gamma,\ \delta,\ \varepsilon,\ \zeta,\ \eta,\ \delta',\ \varepsilon',\ \zeta',\ \eta';$$

and the units

$$\begin{array}{lll}
\alpha\,\beta\,\varepsilon'\,\underset{\cdot}{\eta}' & \underset{\cdot}{\beta}\,\gamma\,\zeta'\,\eta' & \alpha\,\beta\,\varepsilon\,\underset{\cdot}{\eta} \\
\alpha\,\beta\,\zeta'\,\eta' & \alpha\,\underset{\cdot}{\beta}\,\zeta\,\zeta' & \alpha\,\beta\,\zeta\,\eta \\
\alpha\,\delta'\,\varepsilon'\,\underset{\cdot}{\eta}' & \underset{\cdot}{\beta}\,\gamma\,\zeta\,\zeta' & \alpha\,\delta\,\varepsilon\,\underset{\cdot}{\eta} \\
\alpha\,\delta'\,\zeta'\,\underset{\cdot}{\eta}' & \underset{\cdot}{\beta}\,\gamma\,\zeta\,\eta & \alpha\,\delta\,\zeta\,\underset{\cdot}{\eta}\ ^{1)}
\end{array}$$

(The significance of the dots will be explained later).

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1) See fig. 1.

Let Δ_3 be the solid ring formed by placing Γ_3 and three arrays congruent to it end to end in cyclical order, the "ends" being $\delta\,\zeta\,\eta + \delta\,\varepsilon\,\eta$ and $\delta'\,\zeta'\,\eta' + \delta'\,\varepsilon'\,\eta'$ in Γ_3, and their correlates in the other arrays.

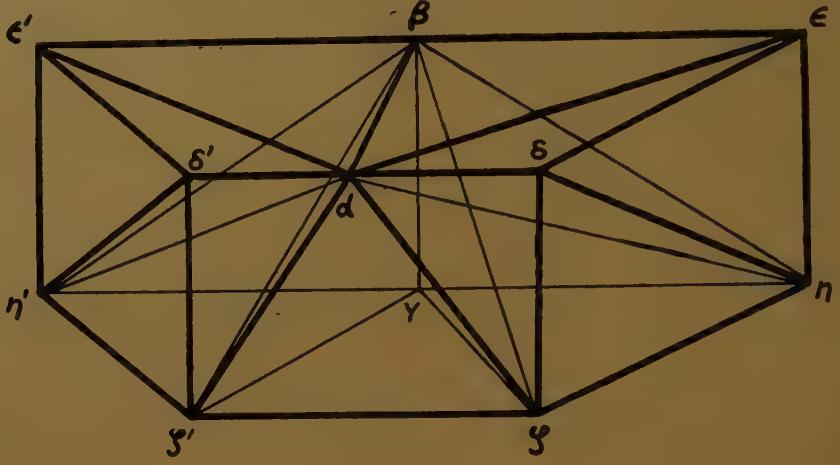

Fig.1:- Γ_3.

Fig. 2 will make the arrangement clear.

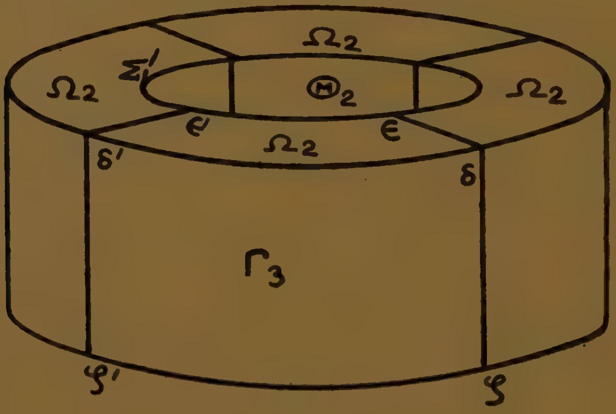

Fig 2 - Δ_3

Part of the boundary of Δ_3 is the "cylinder" Θ_2, formed by adding together the four "rectangles" of the type $\beta\,\varepsilon\,\eta + \beta\,\gamma\,\eta + \beta\,\varepsilon'\,\eta' + \beta\,\gamma\,\eta'$; and the boundary of Θ_2 is made up of two circles, viz. Σ_1, (the sum of the four 1-elements of the type $\gamma\,\eta + \gamma\,\eta'$), and Σ'_1, (the sum of the 1-elements of the type $\beta\,\varepsilon + \beta\,\varepsilon'$).

Let σ and τ be two new vertices, and consider the array, E_3, defined to be $\Delta_3 + \sigma\,(\Theta_2 + \tau\Sigma_1)$.

a. E_3 is a 3-element.

Let Ω_2 be the sum of the four 2-elements of type $\alpha\beta\varepsilon + \alpha\delta\varepsilon + \alpha\beta\varepsilon' + \alpha\delta'\varepsilon'$, and let ω be a new vertex. Then

$$E_3 + \omega\,(\Omega_2 + \sigma\Sigma'_1) \xrightarrow[2]{} \omega\,(\Omega_2 + \sigma\Sigma'_1).$$

For the units of $\sigma\tau\Sigma_1$ can be removed according to the order of their edges in Σ_1; then the units of $\sigma\,\Theta_2$ in the order $\sigma\beta\gamma\eta$, $\sigma\beta\varepsilon\eta$, $\sigma\beta\gamma\eta'$, $\sigma\beta\varepsilon'\eta'$, etc.; and then the units of Γ_3 in the following order:

1. $\beta\gamma\zeta\eta$ $(\gamma\eta)$
2. $\beta\gamma\zeta\zeta'$ $(\gamma\zeta)$
3. $\alpha\beta\zeta\zeta'$ $(\zeta\zeta')$
4. $\alpha\beta\zeta\eta$ $(\beta\zeta)$
5. $\alpha\delta\zeta\eta$ $(\alpha\zeta)$
6. $\alpha\beta\varepsilon\eta$ $(\beta\eta)$
7. $\alpha\delta\varepsilon\eta$ $(\alpha\eta)$
8. $\beta\gamma\zeta'\eta'$ (γ)
9. $\alpha\beta\zeta'\eta'$ $(\beta\zeta')$
10. $\alpha\delta\zeta'\eta'$ $(\alpha\zeta')$
11. $\alpha\beta\varepsilon'\eta'$ $(\beta\eta')$
12. $\alpha\delta'\varepsilon'\eta'$ $(\alpha\eta')$

It will be verified that just before any one of these twelve moves the component which appears after the name of the unit to be removed is free, while the opposite component is interior to what remains of $E_3 + \omega\,(\Omega_2 + \sigma\Sigma'_1)$.

The reduction is completed by dismantling in the same way the other three blocks making up Δ_3.

Now $\Omega_2 + \sigma\Sigma'_1$ is clearly a 2-element: the method of reducing it to a 2-simplex is obvious. It follows that $\omega\,(\Omega_2 + \sigma\Sigma'_1)$ and therefore also $E_3 + \omega\,(\Omega_2 + \sigma\Sigma'_1)$ are 3-elements. But $\omega\,(\Omega_2 + \sigma\Sigma'_1)$ has the 2-element $\Omega_2 + \sigma\Sigma'_1$ in common with the remainder, E_3, of $E_3 + \omega\,(\Omega_2 + \sigma\Sigma'_1)$. Hence, (*F II* Theorem 8*b*), E_3 is a 3-element.

b. E_3 contains no detachable unit.

E_3 has clearly no internal vertex, and it will be verified that no unit has more than one face in the boundary [1]).

---

[1]) In the original specification of Γ_3 every face belonging to $\overline{E_3}$ is indicated by a dot below the opposite vertex of the unit containing it. All other faces of Γ_3 belong to two units of Γ_3, or to $\sigma\Theta_2$, or to an array congruent to Γ_3,

ERRATA.

page 1095, line 1 from top, for "Rott", read: "Rotti".
„ 1098, „ 15 „ „ „ "by rotating of", read: "by rotating".
„ 1098, „ 15 from bottom, for "which diverge in the placoliths", read: "which in the placoliths diverge".
„ 1104, „ 4 from top, for "very circumstances", read: "very special circumstances".

DATE DUE

GAYLORD

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